Chapter 6: Isotopes

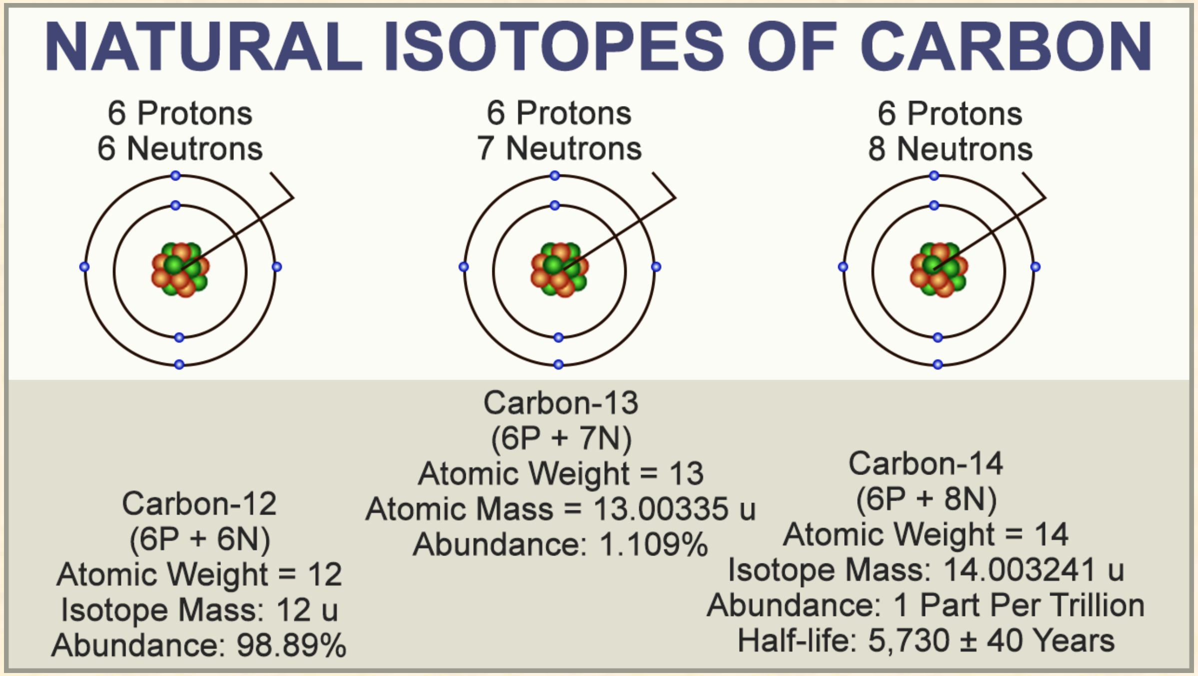

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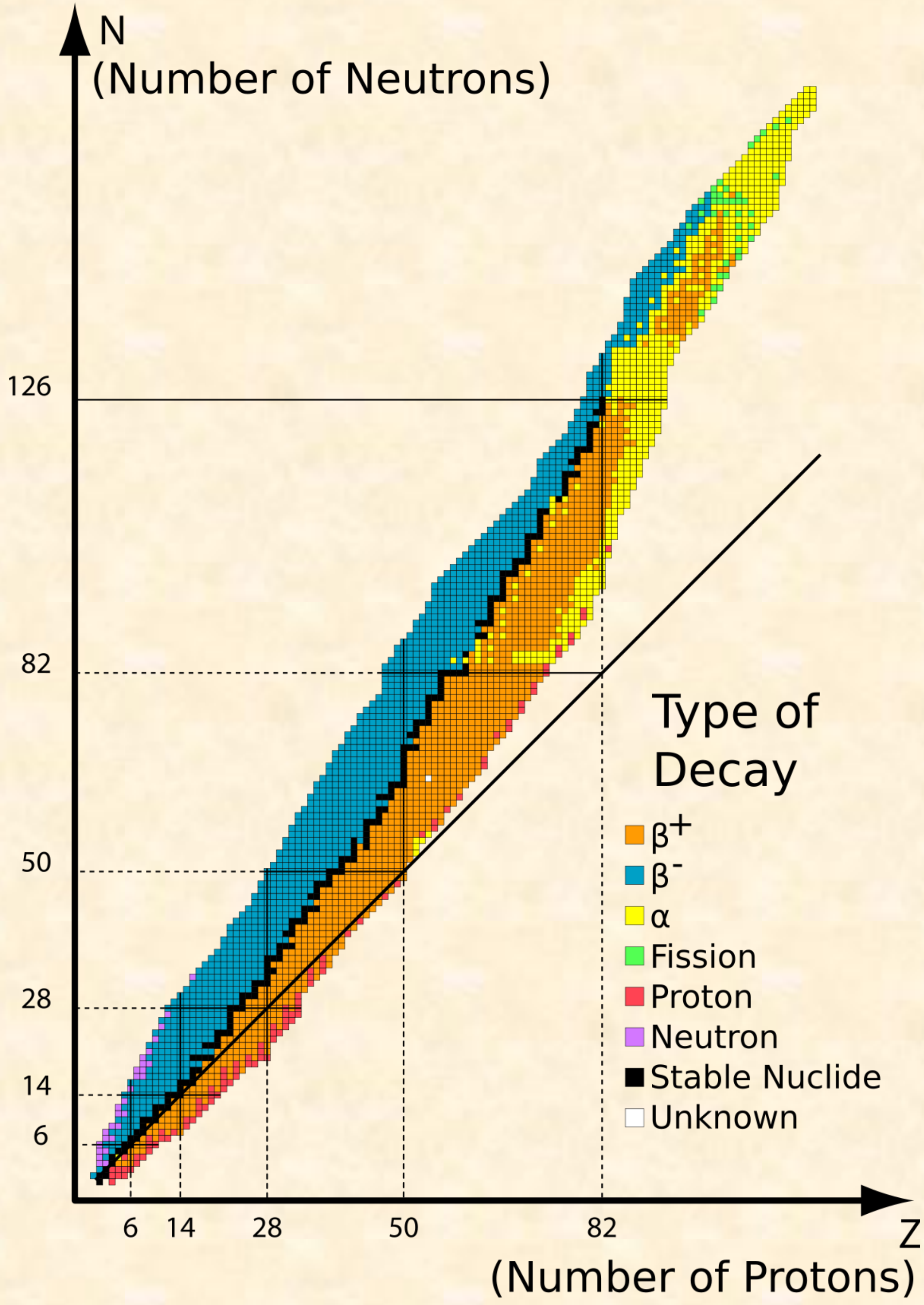
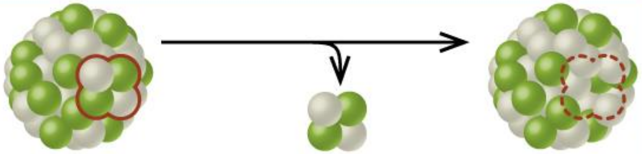
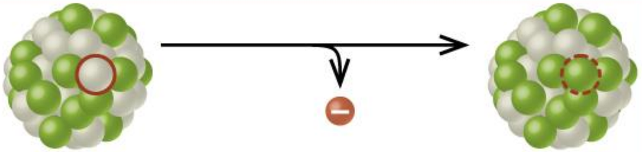
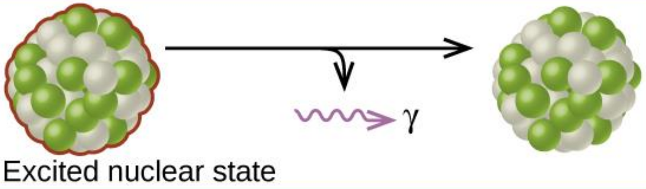
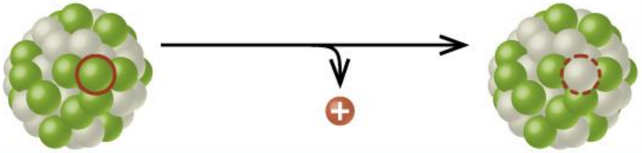
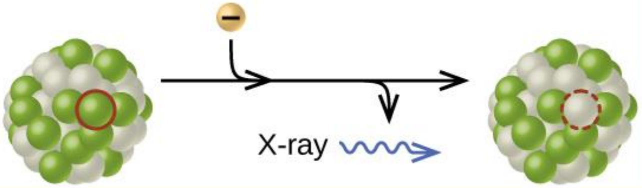
Chart of the Nuclides
Stable versus
Radioactive Isotopes

Note the very narrow band of isotopic stability. Once a nucleus leaves this band, usually because of the addition of neutrons, it becomes radioactive.



Types of Radioactive Decay

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$^{A}_{Z}X \quad ^{4}_{2}He + ^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	$^{A}_{Z}X \quad ^{0}_{-1}e + {}_{Z+1}^{A}Y$		A: unchanged Z: increase by 1
Gamma decay	$^{A}_{Z}X \quad ^{0}_{0}\gamma + ^{A}_{Z}Y$		A: unchanged Z: unchanged
Positron emission	$^{A}_{Z}X \quad ^{0}_{+1}e + {}_{Y-1}^{A}Y$		A: unchanged Z: decrease by 1
Electron capture	$^{A}_{Z}X \quad ^{0}_{-1}e + {}_{Y-1}^{A}Y$		A: unchanged Z: decrease by 1

Radioactive Decay and Growth

The decay of a radioactive isotope is a first-order reaction and can be written:

$$dN/dt = -\lambda N$$

Where N is the number of unchanged atoms at the time t and λ is the radioactive decay constant.

This equation can be rewritten as:

$$N = N_o e^{-\lambda t}$$

Where N_o is the number of atoms present at t = 0. This is the basic form of the radioactive decay equation.

Half-life: the length of time that it takes for half of the atoms to spontaneously decay.

$$t_{1/2} = \ln 2 / \lambda = 0.693 / \lambda$$

The radioactive decay equation can also be written in terms of activity.

$$A = A_o e^{-\lambda t}$$

Where A is the activity at some time t, and A_o is the activity at $t = 0$.

Rearranging this equation and solving for t yields:

$$t = 1/\lambda \ln (A_o/A)$$

In practice, it is often easier to consider radioactive decay in terms of a radioactive parent and radioactive progeny (daughter).

**For any closed system, the number of progeny atoms plus the number of parent atoms remaining must equal the total number of parent atoms at the start. Solving for time yields the following equation:

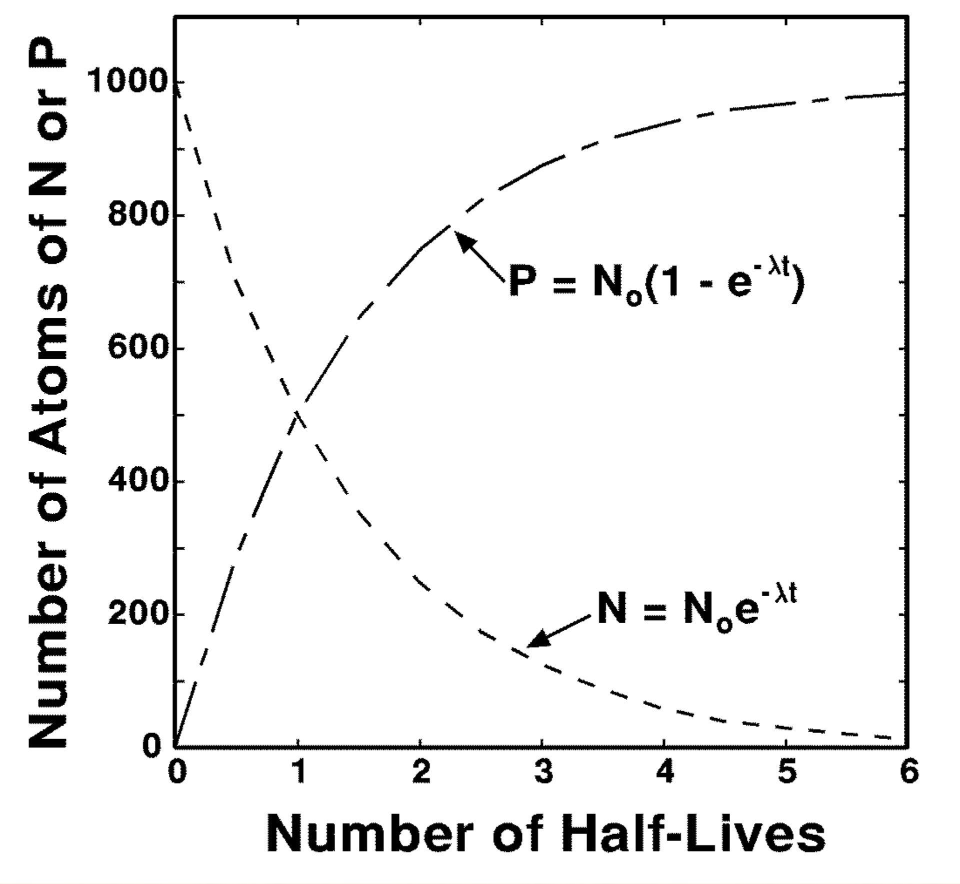
$$t = 1/\lambda \ln[1 + (P/N)]$$

Where N = the number of parent atoms and P = the number of progeny atoms produced.

The number of radioactive progeny can be determined from the following formula:

$$P = N_o(1 - e^{-\lambda t})$$

With the passing of time, the radioactive parent atoms will decline and the radioactive progeny will increase.



Measurement of Radioactivity

Becquerel (Bq) is the basic measurement of radioactivity. 1Bq = 1.000 disintegrations per second.

Curie (Ci) another commonly used measurement of radioactivity. 1Ci = 3.700 x 10^{10} disintegrations per second. A ***picocurie*** is 1 x 10^{-12} curies.

Gray (Gy): the unit used in the study of the chemical and biological effects of radiation. A dose of 1Gy deposits 1 joule of energy per kilogram of material.

Rad: another often-used unit where 1Gy = 100 rad.

The biological effects of radiation are due to changes in the chemistry of the cells. These changes are caused by ionization, excitation, dissociation and atomic displacement due to the passage of the radiation through the cells.

The **sievert (Sy)** is the unit of radiation dosage used to measure the biological effects of radiation.

In the past, the rem (roentgen equivalent man) was the commonly used unit, where 1 Sy = 100rem.

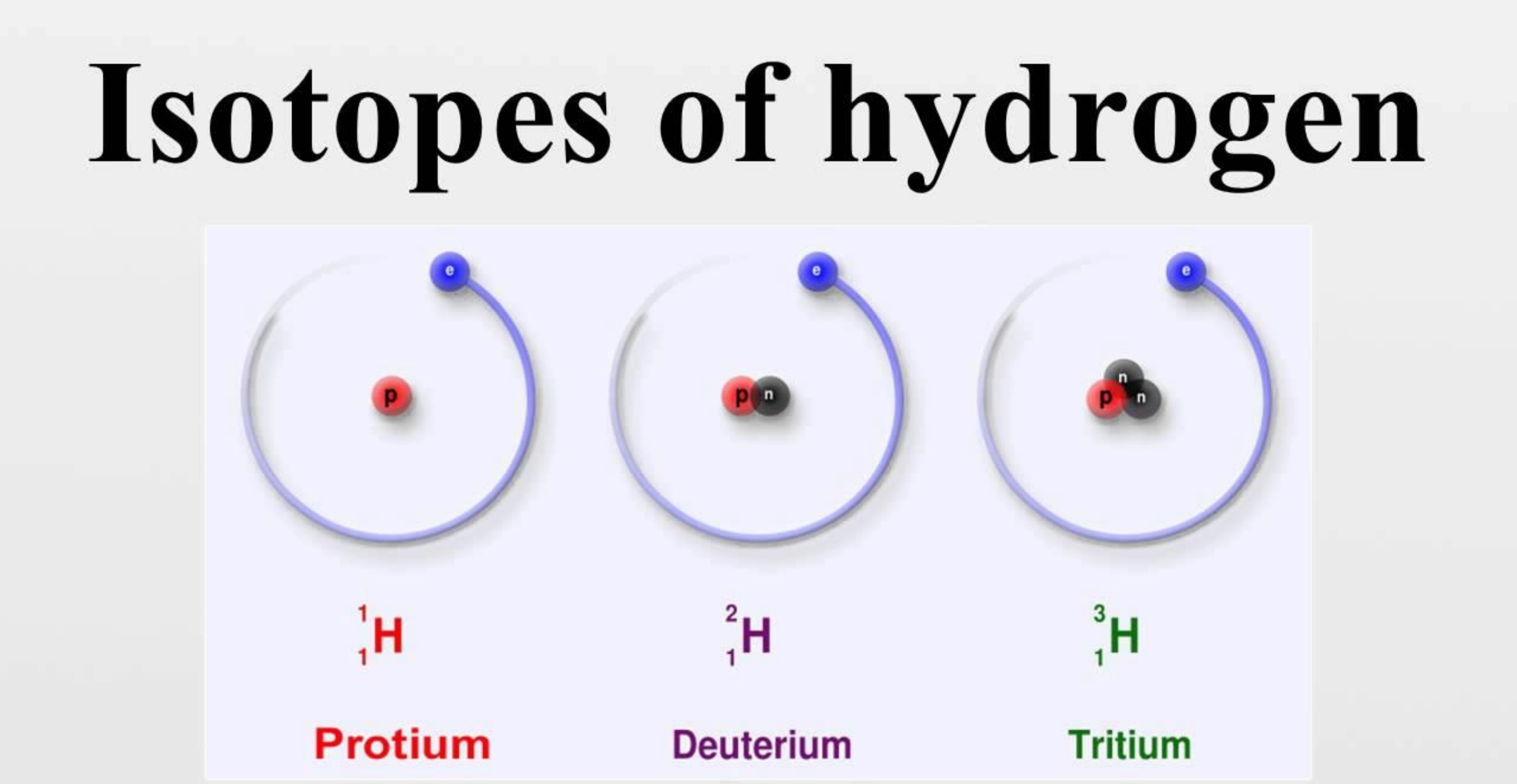
The **relative biological effectiveness (RBE)** is a measure of the ability of various types of radiation to cause ionization in biological materials. The dosage in sieverts is equal to the dosage in grays multiplied by the RBE.

Table 6–3 RBE Values for Various Types of Radiation*

Radiation	RBE
X and γ rays	1
Beta rays and electrons	1
Thermal neutrons	2
Fast neutrons	10
Protons	10
Alpha particles	20
Heavy ions	20

Tritium dating

There are three isotopes of hydrogen: ^{1}H, ^{2}H (deuterium), and ^{3}H (tritium), with average terrestrial abundances (in atomic %) of 99.985, 0.015 and $<10^{-14}$ respectively.



https://en.wikipedia.org/wiki/File:Protium_deuterium_tritium.jpg

Tritium is radioactive and has a half-life of $t_{½} = 12.43$ years. This means it is used to date sample that are less than 50 years old.

Tritium is produced in the upper atmosphere by the bombardment of nitrogen with cosmic-ray produced neutrons.

$$^{14}_{7}N + n \rightarrow 3\ ^{4}_{2}He + \ ^{3}_{1}H$$

The production rate is 0.5 ± 0.3 atoms cm^{-2} sec^{-1}

Tritium abundances are measured in several ways:

tritium unit (TU) = 1 tritium atom per 10^{18} hydrogen atoms

dpm L^{-1} = disintegrations per minute per liter

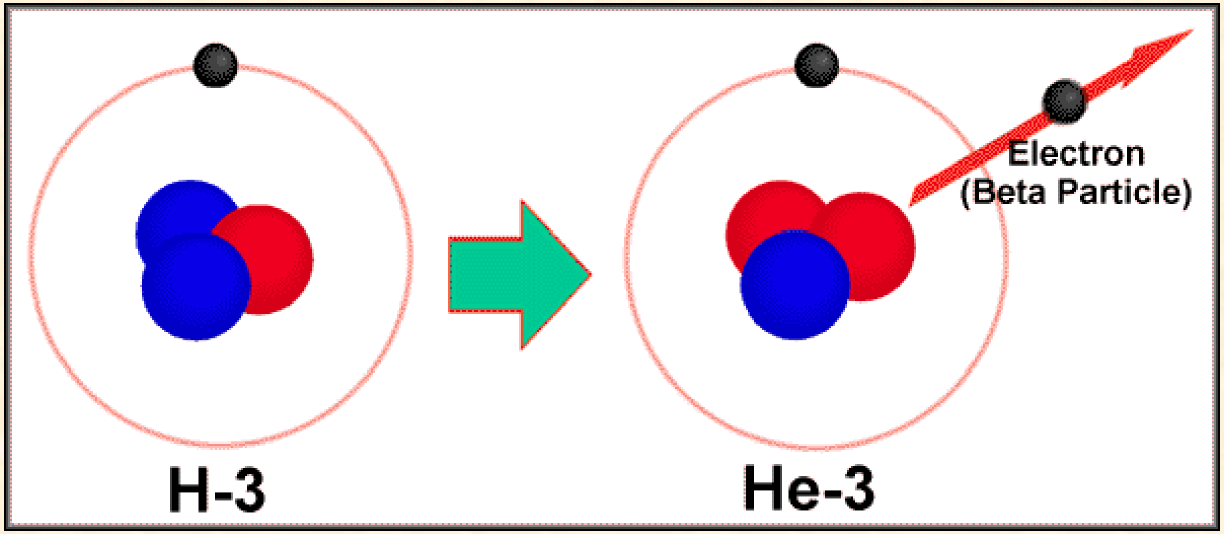
pCi L^{-1} picocuries per liter (of water.)

1TU = 7.1 dpm L^{-1} = 3.25 pCi L^{-1}

From the onset of of atmospheric testing of fusion bombs in 1952, until the signing of the Atmospheric Test Ban Treaty in 1963, bomb- produced tritium was the major source of tritium. Prior to the testing of fusion devices, the tritium content of precipitation was probably between 2 and 8TU. A peak of several thousand TU was recorded in the northern hemisphere precipitation in 1963.

Event dating describes the marking of a specific period where the abundances of an isotope are uncharacteristically elevated or diminished. For example, groundwaters that were recharged between 1952 and 1963 will have a distinctive signature indicating an increase in ^3H production.

Tritium decays through β- emission. This means that the parent material is ^3H and the progeny material is ^3He.



Given $\lambda_T = 5.575 \times 10^{-2}\ y^{-1}$, if through sampling ground water you find $^3H = 25TU$ and $^3He = 0.8TU$, what time has passed since that groundwater was recharged (at the surface)?

$$\text{Recall: } t = 1/\lambda \cdot \ln[1 + (P/N)]$$

$$t = 17.937 \cdot \ln[1 + (0.8/25)] = 0.6\ y$$

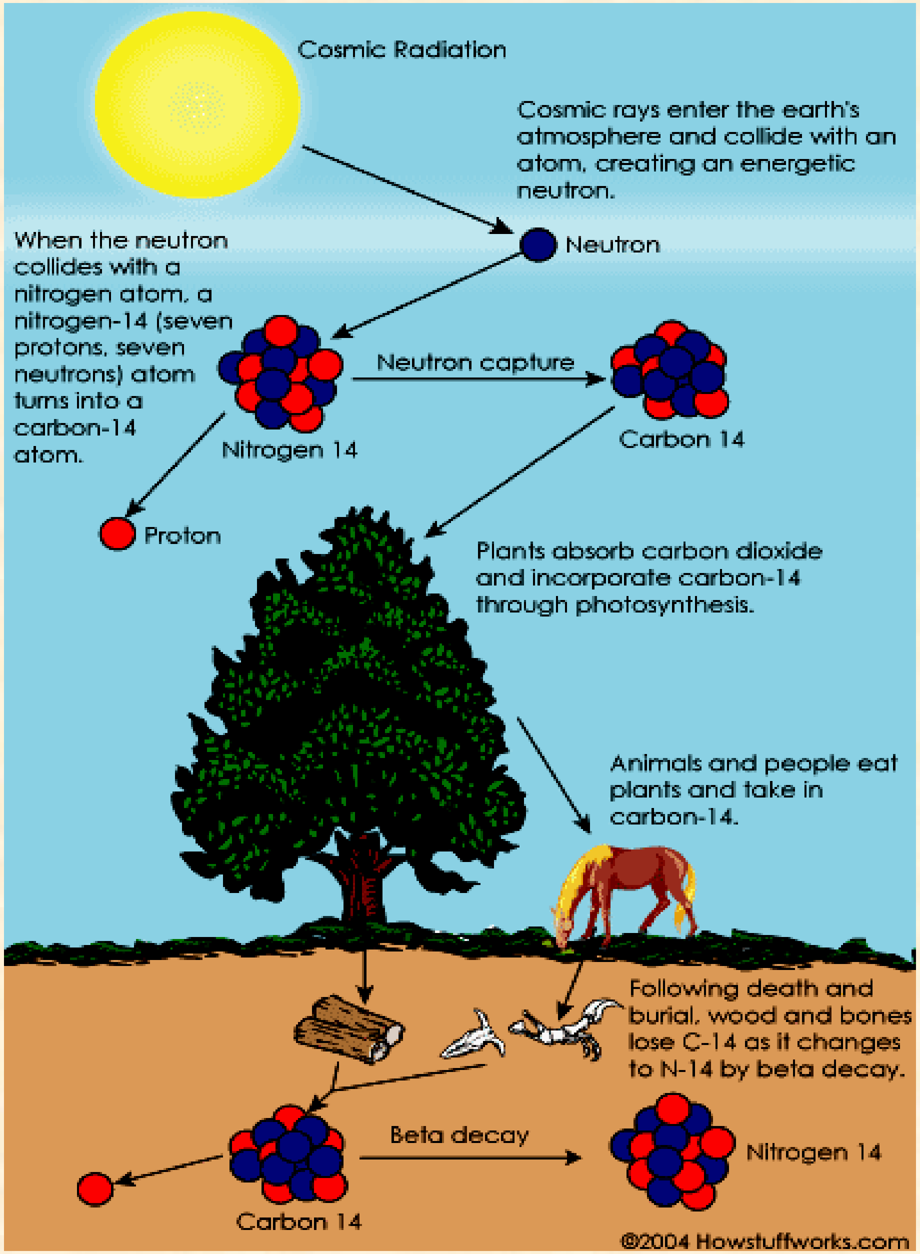
Carbon – 14 Dating

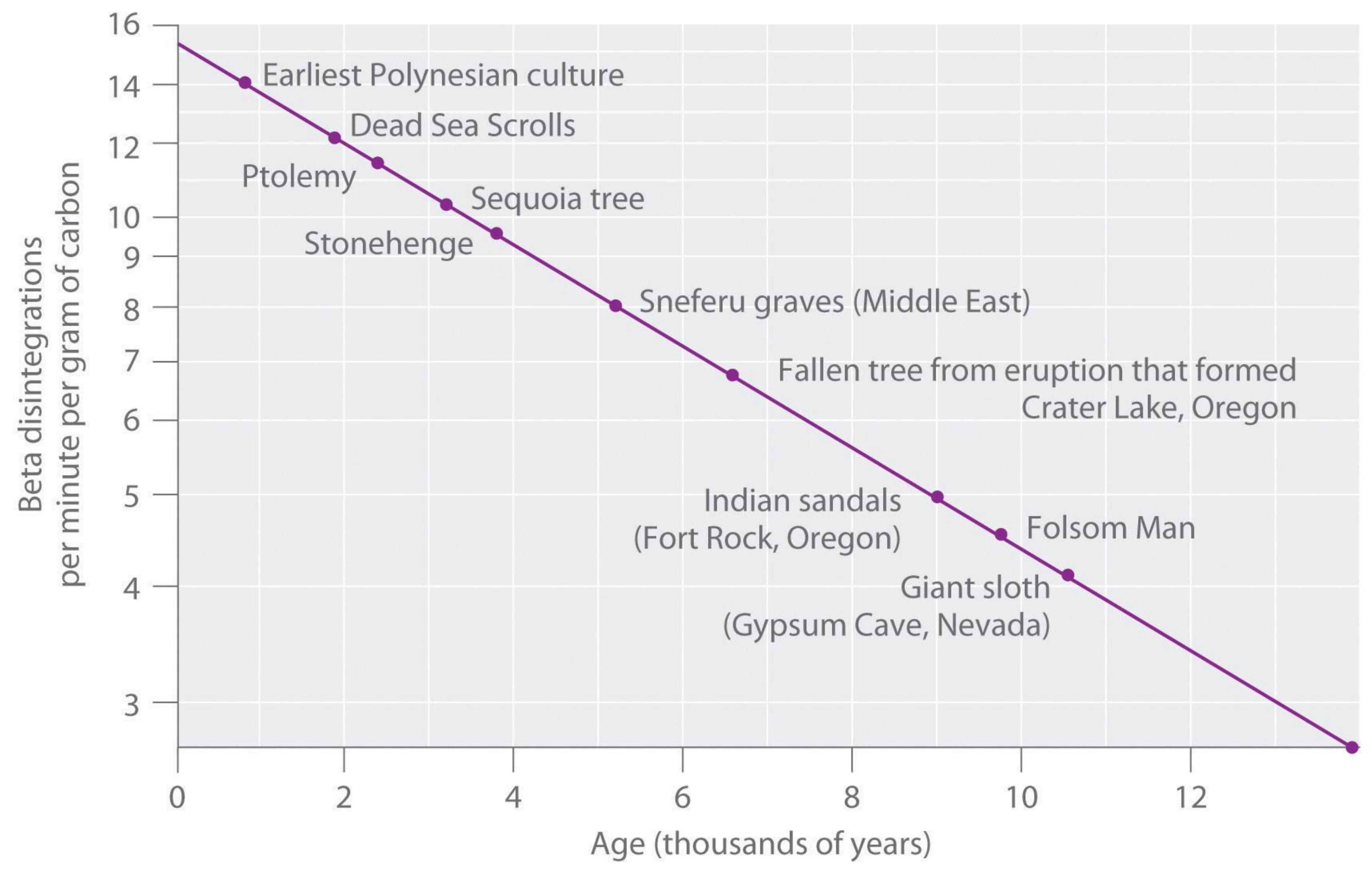
^{14}C has been used for dating samples that are roughly 50,000 years old or younger (accelerator mass spectrometry ups the usage to 100,000 years). There are 3 isotopes of carbon: ^{12}C, ^{13}C, & ^{14}C, with average terrestrial abundances of 98.90, 1.10, and $<10^{-10}$, respectively. ^{14}C is the only radioactive carbon isotope with a half-life of 5,730 years.

$$^{14}_{7}N + n \rightarrow \, ^{1}_{1}H + \, ^{14}_{6}C$$

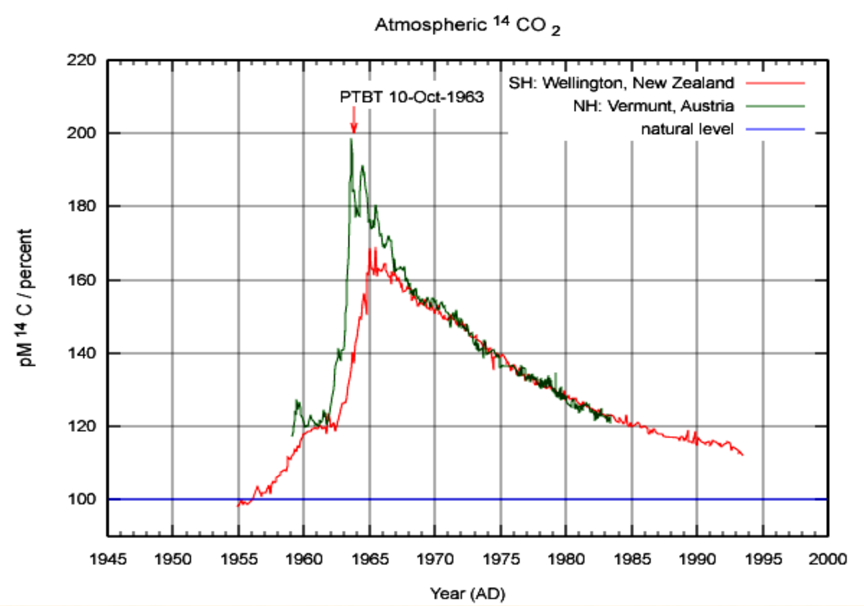
$$^{14}_{6}C \rightarrow \, ^{14}_{7}N + \beta^{-} + \overline{\nu} + Q$$

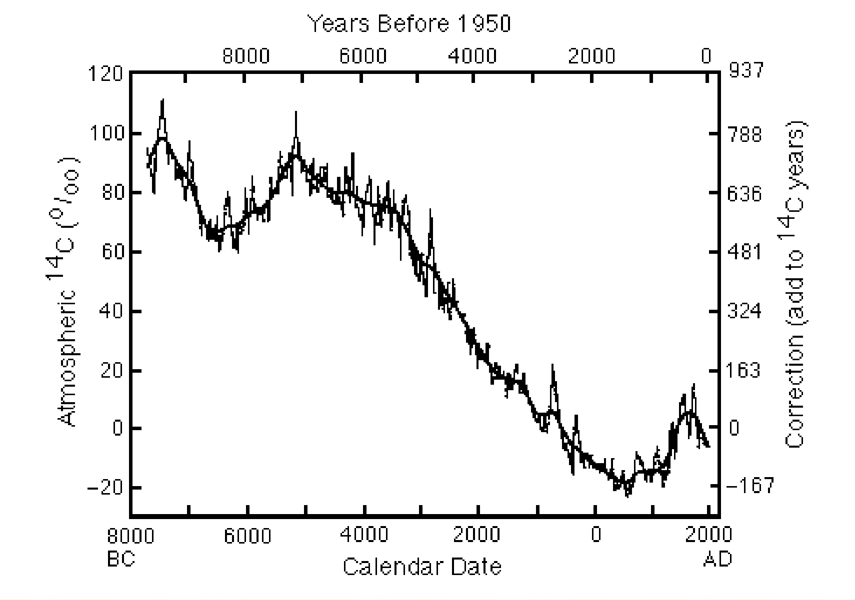
$$t = \frac{1}{1.209\ x\ 10^{-4}} \ln\left(\frac{Ao}{A}\right)$$



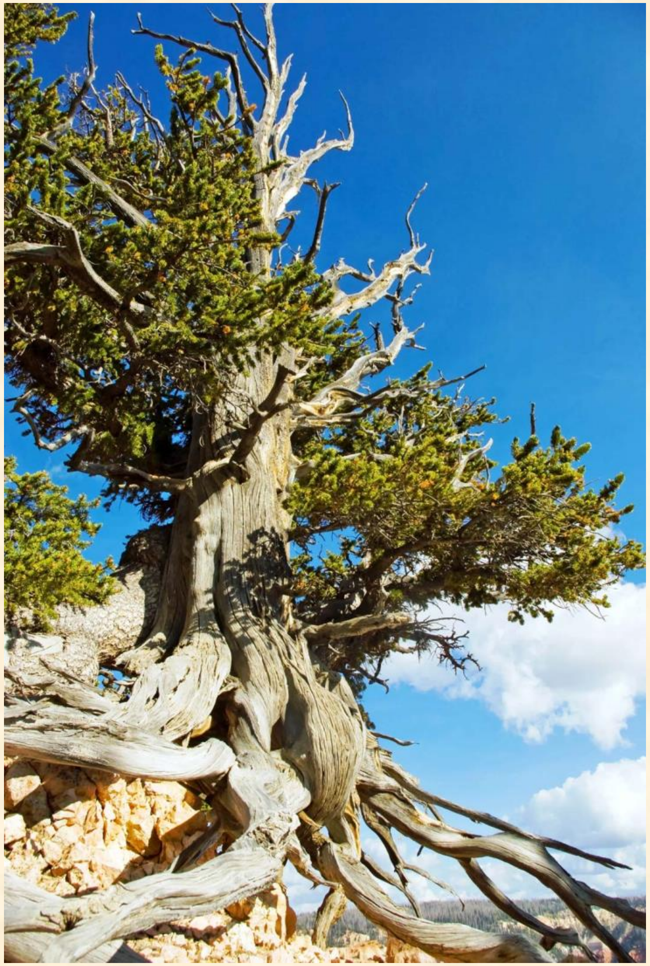

Beta disintegrations per minute per gram of carbon
16
14
12
10
9
8
7
6
5
4
3
Earliest Polynesian culture
Dead Sea Scrolls
Ptolemy
Sequoia tree
Stonehenge
Sneferu graves (Middle East)
Fallen tree from eruption that formed Crater Lake, Oregon
Indian sandals (Fort Rock, Oregon)
Folsom Man
Giant sloth (Gypsum Cave, Nevada)
0
2
4
6
8
10
12
Age (thousands of years)

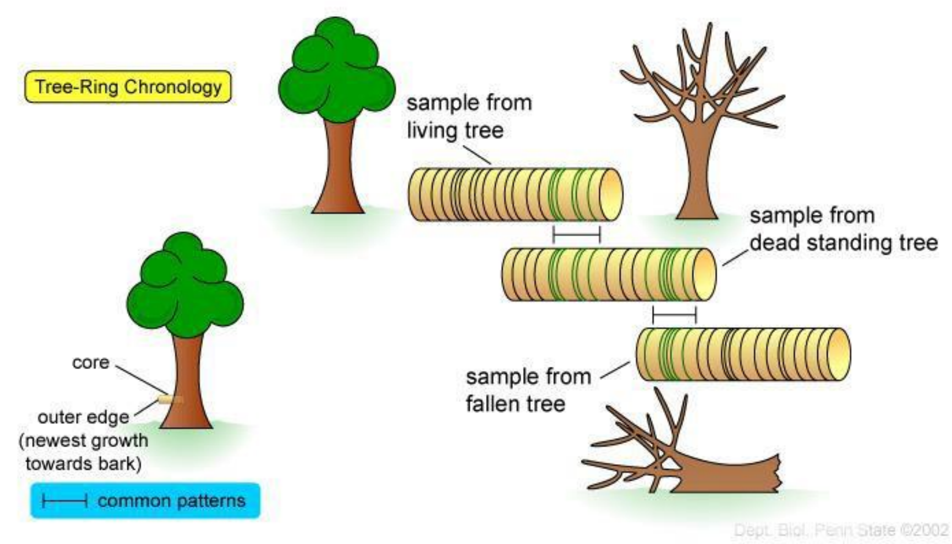
In order to use ^{14}C for geochronology, it is assumed that the atmosphere is in secular equilibrium with respect to ^{14}C. Meaning that the rate at which ^{14}C is produced by cosmic ray flux is equal to the rate of decay of ^{14}C, so the abundance of ^{14}C in the atmosphere remains constant. However, for a variety of reasons, the abundance of ^{14}C has not remained constant over time. These variations need to be accounted for when using this dating method.

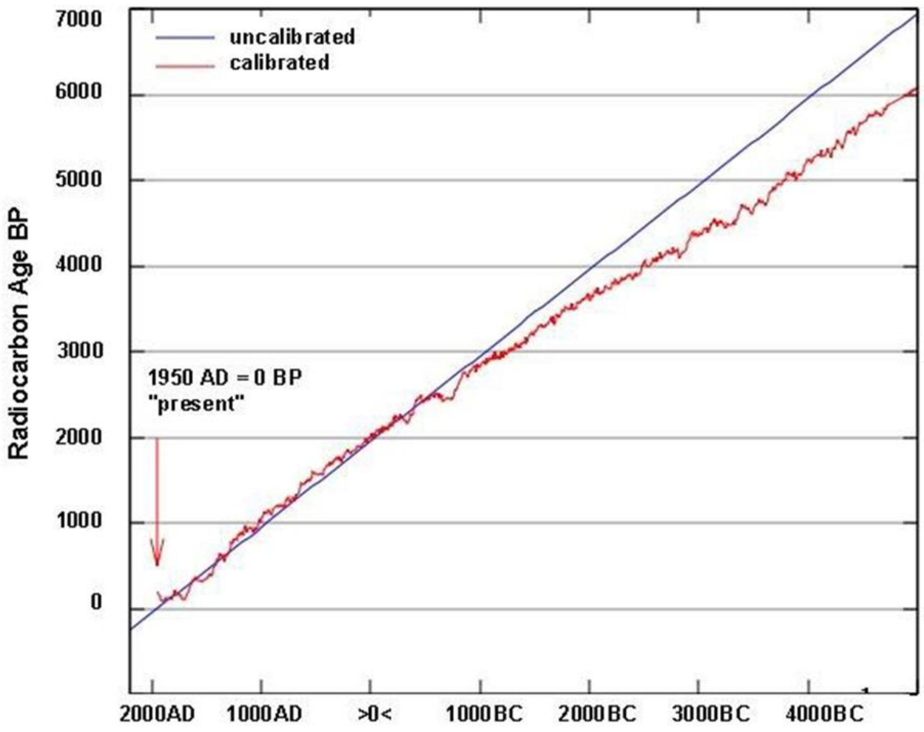




In order to calibrate the C-14 time scale one must use carbon-containing materials of known age. A popular choice is the bristlecone pine, the oldest of which has an age of almost 5,000 years.







U-Series Disequilibrium Methods of Dating

For a system that has been closed for a sufficiently long time, secular equilibrium will be achieved and the relative abundance of each isotope will be constant.

When the system enters disequilibrium due to separation of either parent or progeny, or subsequent decay, the reestablishment of equilibrium can be used as a dating method.

For example, when ^{234}U decays to ^{230}Th in sea water, the ^{230}Th is rapidly removed from sea water because, unlike uranium, thorium is very insoluble (reactive). In this case, the ^{230}Th that accumulates in the sediments is said to be unsupported, as it is now separated from its parent isotope.

Table 6-1. Uranium decay series*

Uranium 238			Uranium 235		
Isotope	Emitted particle	Half-life	Isotope	Emitted particle	Half-life
${}^{238}_{92}\mathrm{U}$	α	4.47 x 10^{9} yrs	${}^{235}_{92}\mathrm{U}$	α	7.038 x 10^{8} yrs
${}^{234}_{90}\mathrm{Th}$	β^-	24.1 days	${}^{231}_{90}\mathrm{Th}$	β^-	1.063 days
${}^{234}_{91}\mathrm{Pa}$	β^-	1.17 min	${}^{231}_{91}\mathrm{Pa}$	α	3.248 x 10^{4} yrs
${}^{234}_{92}\mathrm{U}$	α	2.48 x 10^{5} yrs	${}^{227}_{89}\mathrm{Ac}$	β^-	21.77 yrs
${}^{230}_{90}\mathrm{Th}$	α	7.52 x 10^{4} yrs	${}^{227}_{90}\mathrm{Th}$	α	18.72 days
${}^{226}_{88}\mathrm{Ra}$	α	1.60 x 10^{3} yrs	${}^{223}_{88}\mathrm{Ra}$	α	11.435 days
${}^{222}_{86}\mathrm{Rn}$	α	3.8235 days	${}^{219}_{86}\mathrm{Rn}$	α	3.96 sec
${}^{218}_{84}\mathrm{Po}$	α	3.10 min	${}^{215}_{84}\mathrm{Po}$	α	1.78 x 10^{-3} sec
${}^{214}_{82}\mathrm{Pb}$	β^-	27 min	${}^{211}_{82}\mathrm{Pb}$	β^-	36.1 min
${}^{214}_{83}\mathrm{Bi}$	β^-	19.9 min	${}^{211}_{83}\mathrm{Bi}$	α	2.14 min
${}^{214}_{84}\mathrm{Po}$	α	1.64 x 10^{-4} sec	${}^{207}_{81}\mathrm{Tl}$	β^-	4.77 min
${}^{210}_{82}\mathrm{Pb}$	β^-	22.3 yrs	${}^{207}_{82}\mathrm{Pb}$		Stable
${}^{210}_{83}\mathrm{Bi}$	β^-	5.01 days			
${}^{210}_{84}\mathrm{Po}$	α	138.38 days			
${}^{206}_{82}\mathrm{Pb}$		Stable			

*Data source: Chart of the Nuclides (1989).

Table 6-2. Thorium decay series*

Isotope	Emitted particle	Half-life
$^{232}_{90}\text{Th}$	α	1.40×10^{10} yrs
$^{228}_{88}\text{Ra}$	β^-	5.76 yrs
$^{228}_{89}\text{Ac}$	β^-	6.15 hr
$^{228}_{90}\text{Th}$	α	1.913 yrs
$^{224}_{88}\text{Ra}$	α	3.66 days
$^{220}_{86}\text{Rn}$	α	55.6 sec
$^{216}_{84}\text{Po}$	α	0.145 sec
$^{212}_{82}\text{Pb}$	β^-	10.64 hr
$^{212}_{83}\text{Bi}$	α (33.7%) β^- (66.3%)	1.009 hr
$^{208}_{81}\text{Tl}$	β^-	3.053 min
$^{212}_{84}\text{Po}$	α	2.98×10^{-7} sec
$^{208}_{82}\text{Pb}$		Stable

*Data source: Chart of the Nuclides (1989).

^{230}Th Dating of Marine Sediments:

As we saw in the last example, ^{230}Th is reactive in the marine environment (i.e., it is rapidly removed from seawater by particles). In fact it has a mean residence time of about 300 years.

Given that the addition and removal of U (^{230}Th's parent) to the ocean is in balance (U has a residence time in seawater of about 1 million years), ^{230}Th is produced at a constant rate. This means that as long as there has been no disruption to the sediment layers on the sea floor, the uppermost layer will represent present-day ^{230}Th deposition to the sediments.

$$\lambda_{^{230}\mathrm{Th}} = 9.217 \times 10^{-6}\,\mathrm{y}^{-1}.$$

$$t = 108{,}495 \ln({}^{230}\mathrm{Th}_{\mathrm{initial}} / {}^{230}\mathrm{Th}_{\mathrm{measured}})$$

Example 6-4

The ^{230}Th activity is measured for a marine sediment core. The top layer of the core has a ^{230}Th activity of 62 dpm. At a depth of 1m, the ^{230}Th activity is 28 dpm. Calculate the age of the sediment at a depth of 1m.

$$t = 108{,}495 \ln(62/28) = 86{,}246 \text{ y}$$

Rate = (sediment thickness / time) = 1m / 86,246 y = 1.16 cm /1000 y.

^{230}Th / ^{232}Th Sediment Dating

This method uses the ratio of these two radioisotopes instead of just ^{230}Th. In this case the age equation is

$$t = 1/\lambda \ln (R_0 / R) = 108{,}495 \ln (R_0 / R)$$

Where……

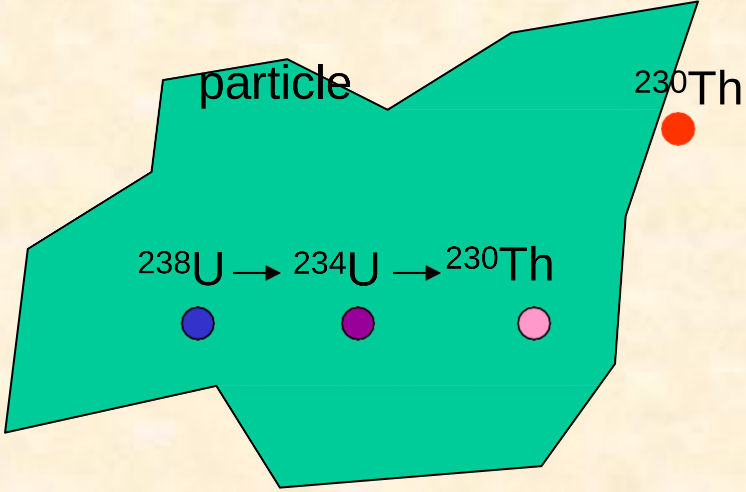
$R = {}^{230}\mathrm{Th} / {}^{232}\mathrm{Th}$ measured

$R_0 = {}^{230}\mathrm{Th} / {}^{232}\mathrm{Th}$ initial

R is also = $({}^{230}\mathrm{Th} / {}^{232}\mathrm{Th})^0 e^{-\lambda t}$

So far the examples have been for ‘unsupported’ activity. We have assumed that parent and progeny are separated.

Supported activity – case where a parent or grandparent was originally present in the sediment. Decay of this parent and/or grandparent contributes to the total activity of the progeny.



^{230}Th ● = Thorium scavenged from the water column = unsupported acitvity

^{230}Th ○ = Thorium produced from ^{238}U in the particle = supported activity

Total activity = ^{230}Th ● + ^{230}Th ○

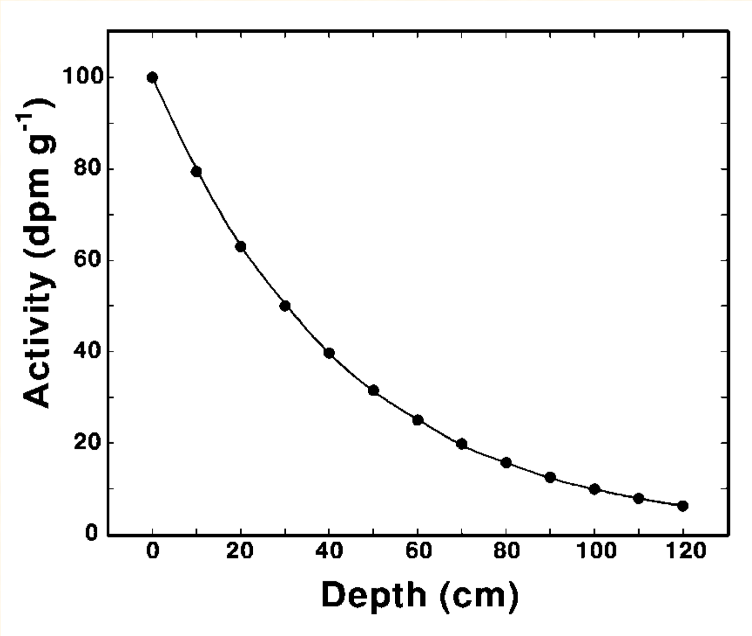
^{230}Th / ^{231}Pa Sediment Dating

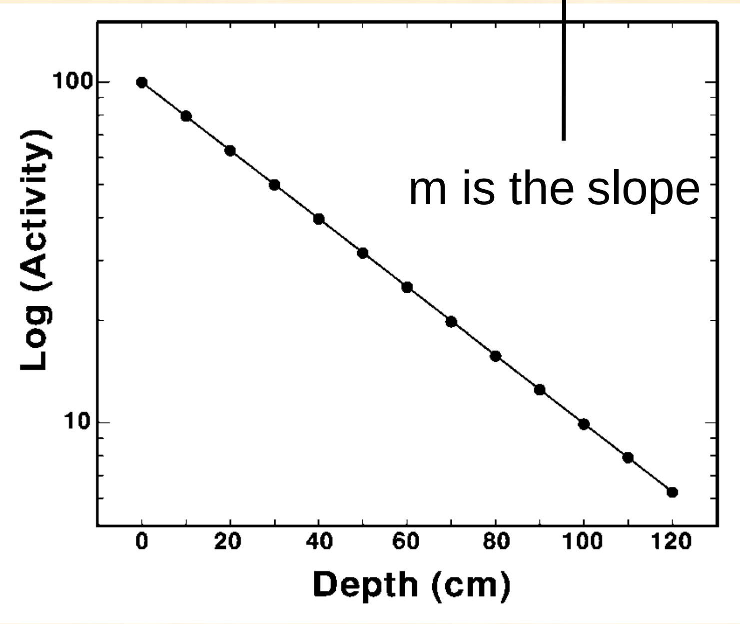
Very similar to the ^{230}Th / ^{232}Th except the half life is shorter, so you can use it for somewhat faster accumulation rates.

Activity and Sediment-Rate Relationships

Radioactive decay is a first-order process (i.e. exponential decay)

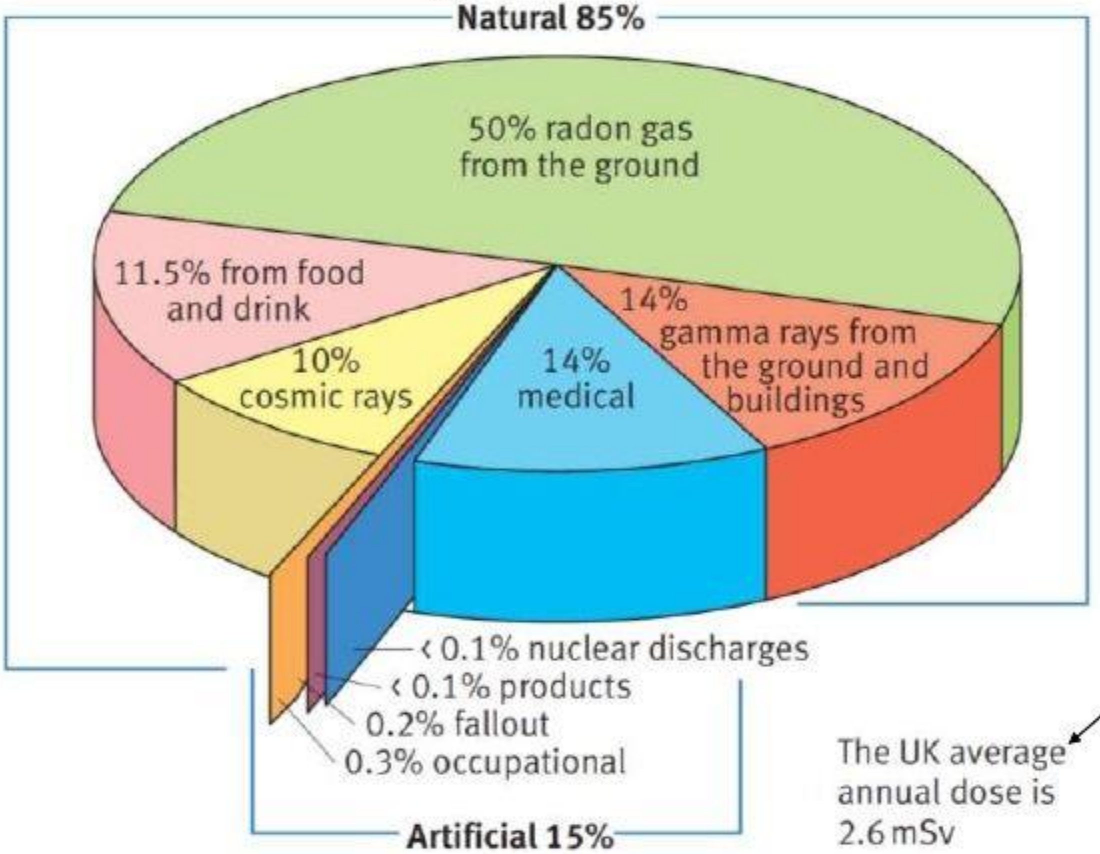
If sedimentation is constant then the sedimentation rate (a) = (λ /-2.303m)



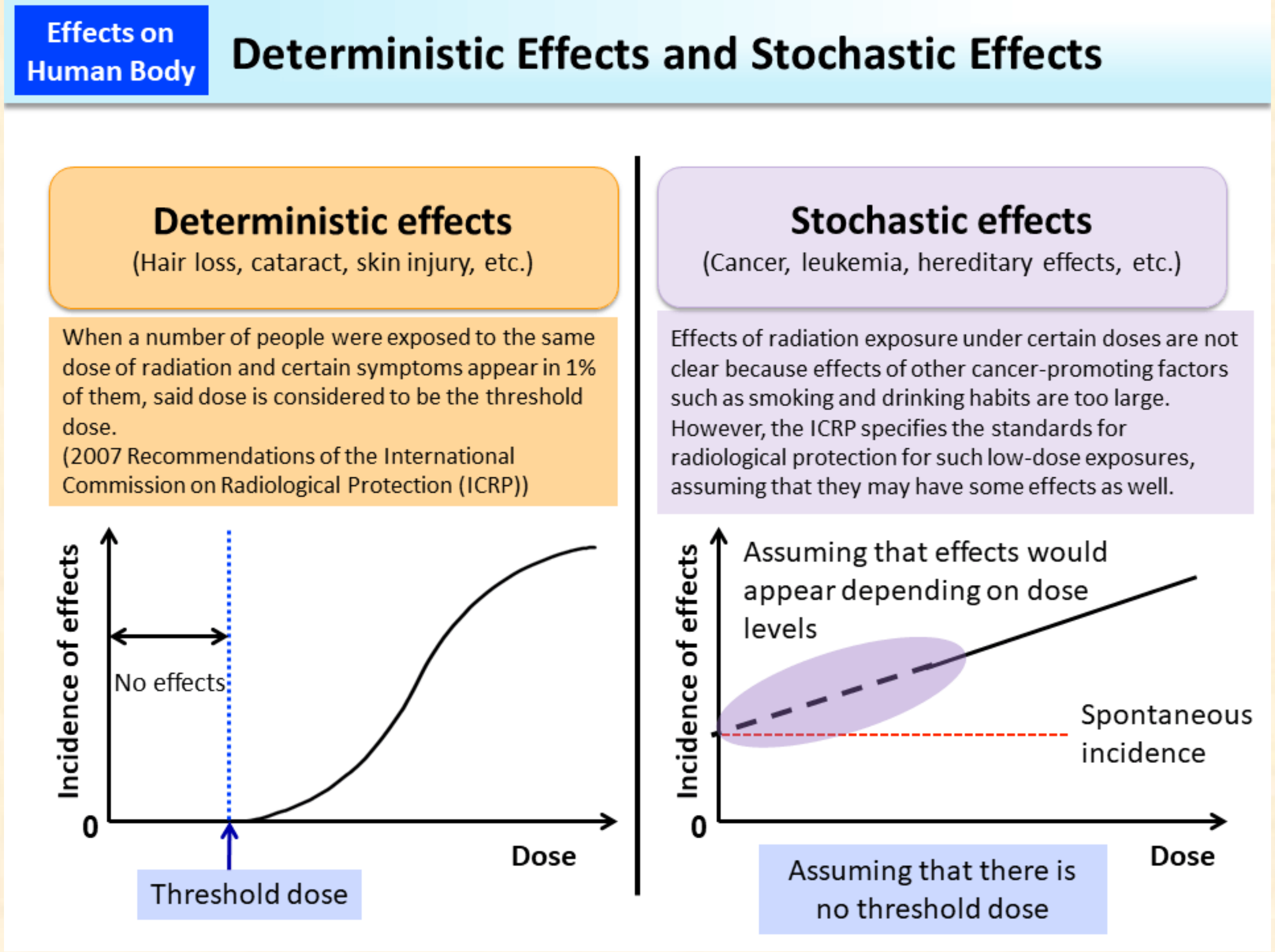


m is the slope

Background Radiation



The dose of radiation is measured in sieverts Sv, or millisieverts mSv.



Effects on Human Body

Deterministic Effects and Stochastic Effects

Deterministic effects

(Hair loss, cataract, skin injury, etc.)

When a number of people were exposed to the same dose of radiation and certain symptoms appear in 1% of them, said dose is considered to be the threshold dose.
(2007 Recommendations of the International Commission on Radiological Protection (ICRP))

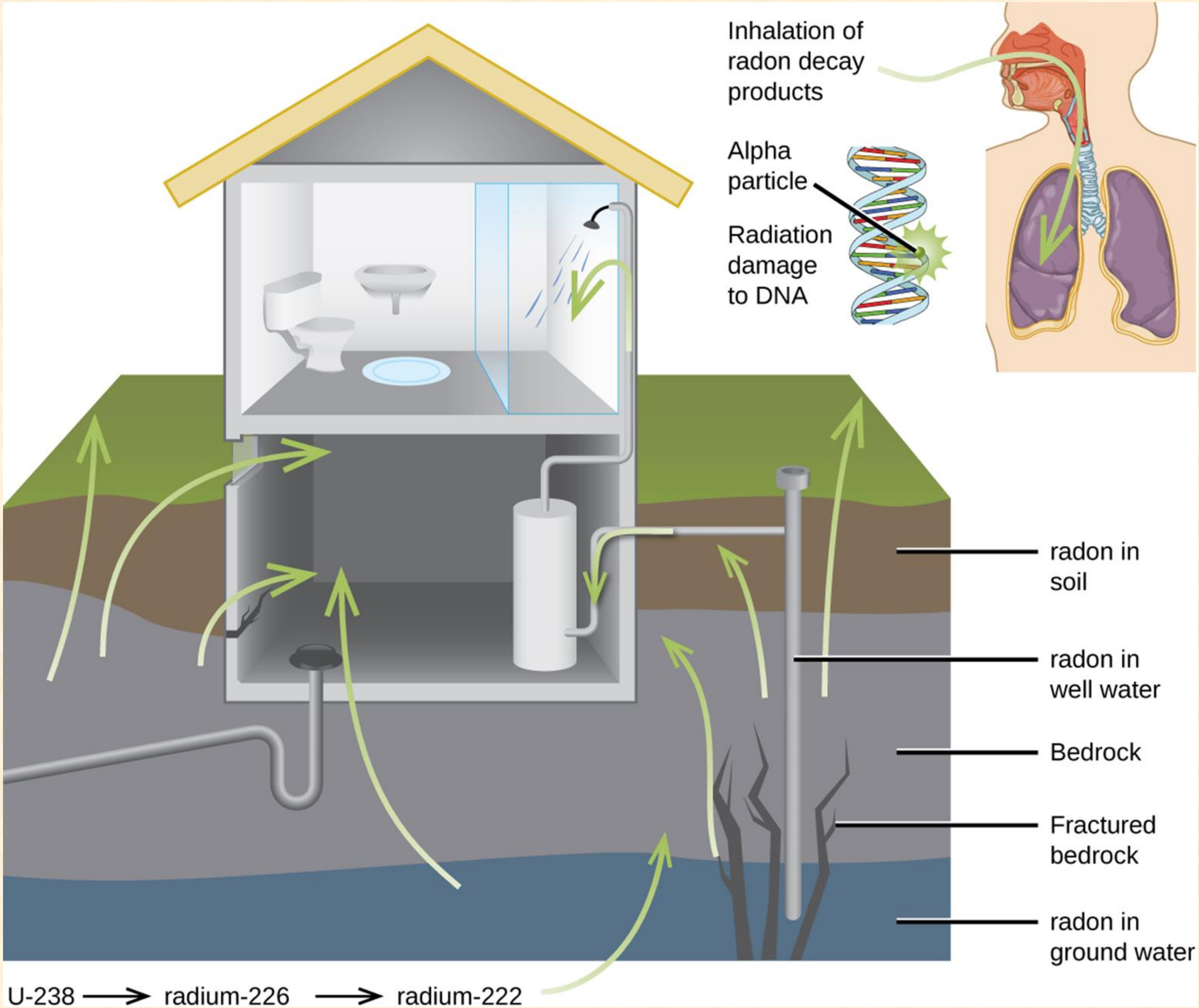
Stochastic effects

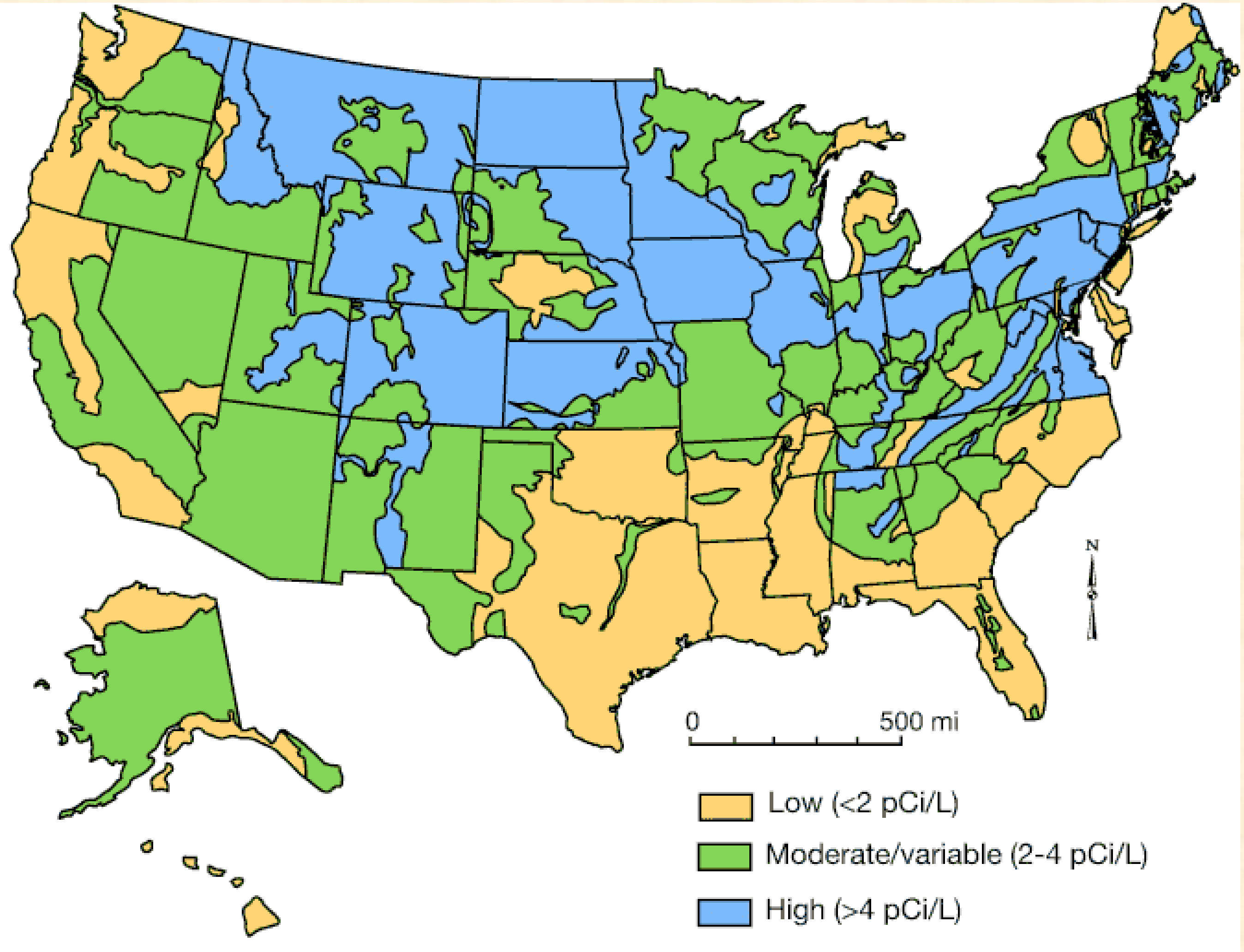
(Cancer, leukemia, hereditary effects, etc.)

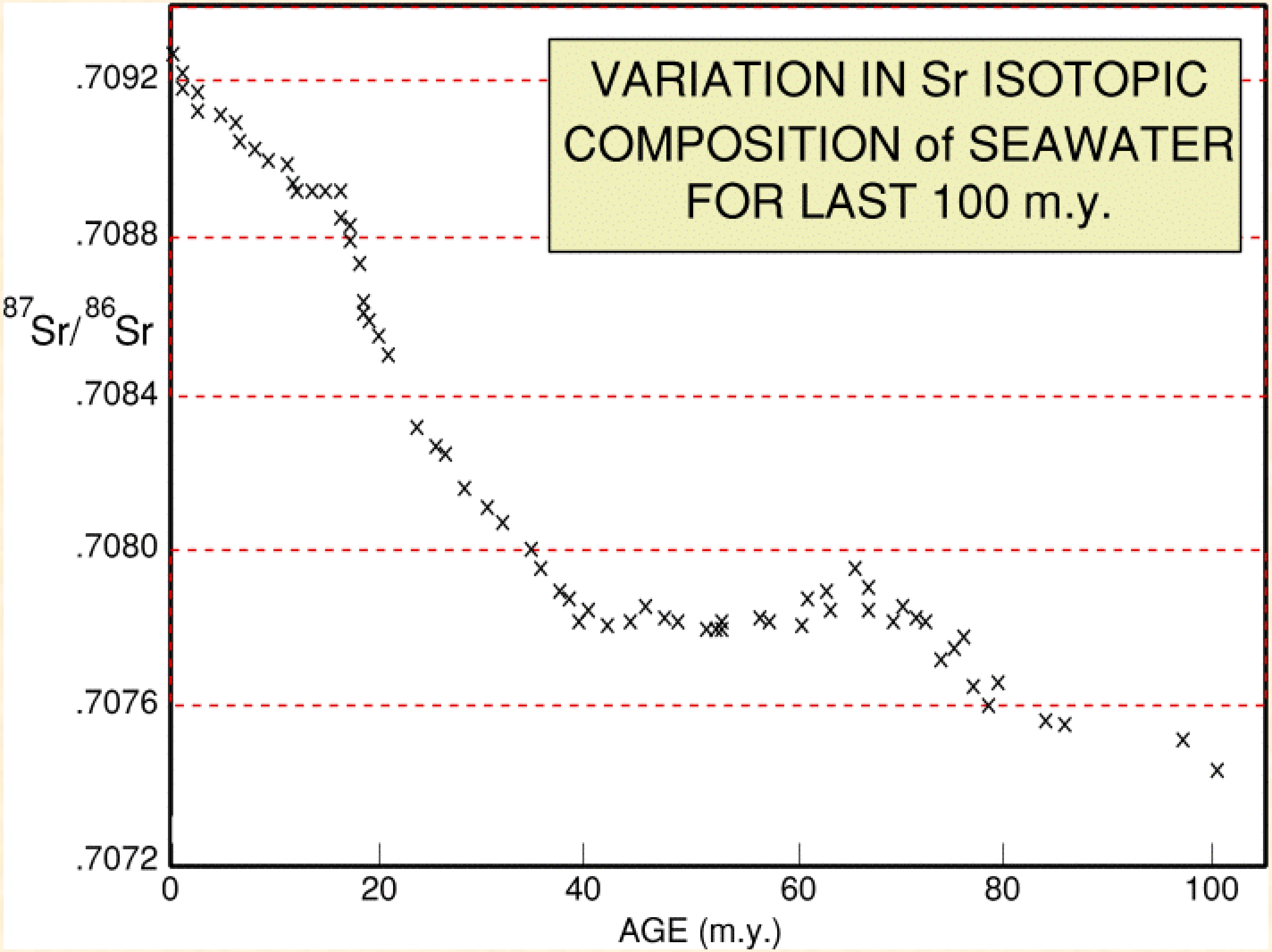
Effects of radiation exposure under certain doses are not clear because effects of other cancer-promoting factors such as smoking and drinking habits are too large. However, the ICRP specifies the standards for radiological protection for such low-dose exposures, assuming that they may have some effects as well.

Deterministic system is a system in which no randomness is involved in the development of future states of the system. Can accurately predict future states.

Stochastic system has a random probability distribution or pattern that may be analyzed statistically but may not be predicted precisely.

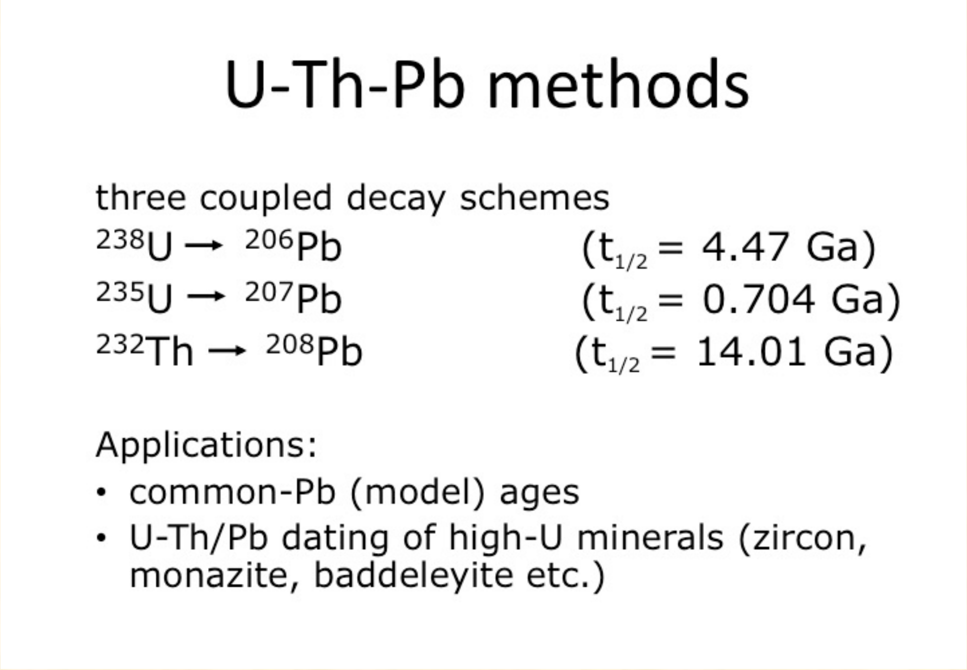

Inhalation of radon decay products
Alpha particle
Radiation damage to DNA
radon in soil
radon in well water
Bedrock
Fractured bedrock
radon in ground water
U-238 → radium-226 → radium-222


0
500 mi
N
🟧 Low (<2 pCi/L)
🟩 Moderate/variable (2-4 pCi/L)
🟦 High (>4 pCi/L)



VARIATION IN Sr ISOTOPIC COMPOSITION of SEAWATER FOR LAST 100 m.y.

U-Th-Pb isotopic systems



U-Th-Pb methods

three coupled decay schemes

$^{238}U \rightarrow {}^{206}Pb$ ($t_{1/2}$ = 4.47 Ga)

$^{235}U \rightarrow {}^{207}Pb$ ($t_{1/2}$ = 0.704 Ga)

$^{232}Th \rightarrow {}^{208}Pb$ ($t_{1/2}$ = 14.01 Ga)

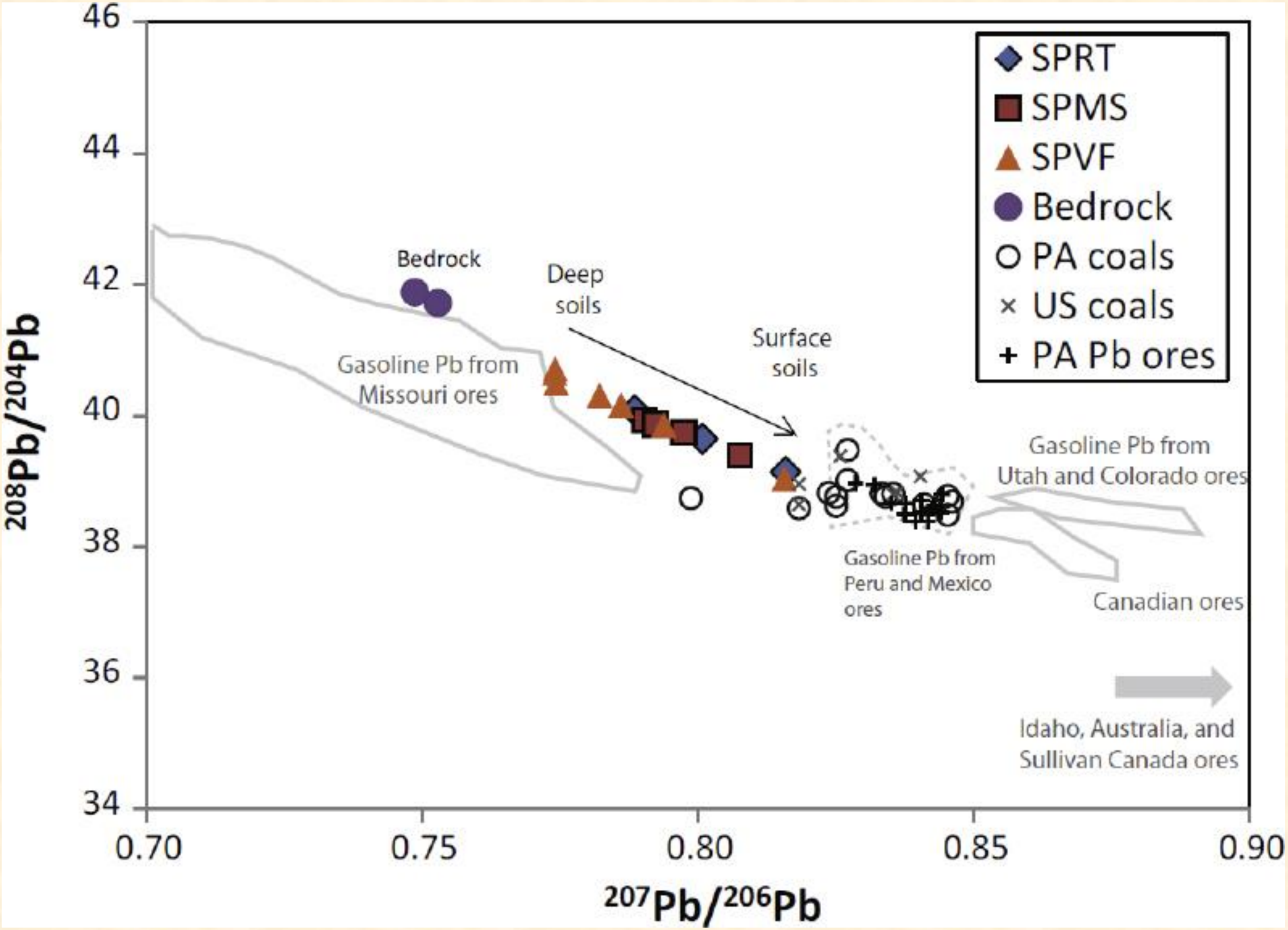
Applications:

- common-Pb (model) ages
- U-Th/Pb dating of high-U minerals (zircon, monazite, baddeleyite etc.)

$$\left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{meas}} = \left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{initial}} + \left(\frac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}\right)(e^{\lambda_{238}t} - 1)$$

$$\left(\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{meas}} = \left(\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{initial}} + \left(\frac{^{235}\mathrm{U}}{^{204}\mathrm{Pb}}\right)(e^{\lambda_{235}t} - 1)$$

$$\left(\frac{^{208}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{meas}} = \left(\frac{^{208}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_{\mathrm{initial}} + \left(\frac{^{232}\mathrm{U}}{^{204}\mathrm{Pb}}\right)(e^{\lambda_{232}t} - 1)$$


46
44
42
40
38
36
34
$^{208}Pb/^{204}Pb$
0.70
0.75
0.80
0.85
0.90
$^{207}Pb/^{206}Pb$
◆ SPRT
■ SPMS
▲ SPVF
● Bedrock
○ PA coals
× US coals
+ PA Pb ores
Bedrock
Deep soils
Surface soils
Gasoline Pb from Missouri ores
Gasoline Pb from Utah and Colorado ores
Gasoline Pb from Peru and Mexico ores
Canadian ores
Idaho, Australia, and Sullivan Canada ores

Stable Isotopes

Do not spontaneously breakdown to form other isotopes

Table 6-6. Average terrestrial abundances of stable isotopes used in environmental studies*

Element	Isotope	Average Terrestrial Abundance (atom %)
Hydrogen	${}^{1}_{1}H$	99.985
	${}^{2}_{1}H$	0.015
Carbon	${}^{12}_{6}C$	98.9
	${}^{13}_{6}C$	1.1
Nitrogen	${}^{14}_{7}N$	99.63
	${}^{15}_{7}N$	0.37
Oxygen	${}^{16}_{8}O$	99.762
	${}^{17}_{8}O$	0.038
	${}^{18}_{8}O$	0.2
Sulfur	${}^{32}_{16}S$	95.02
	${}^{33}_{16}S$	0.75
	${}^{34}_{16}S$	4.21
	$_{16}$*subp*36S	0.014

*Data source: IUPAC (1992).

Isotopic Fractionation – partitioning of isotopes during phase change or reactions. Partitioning is proportional to the masses of the isotopes.

Equilibrium Fractionation: forward and backward reaction rates are equal for each isotope.

Bi-directional reactions at equilibrium (like water vapor over water) Lighter isotopes in the gas phase (lighter isotopes = more kinetic energy).

Example: evaporation of water in a closed space

Kinetic Fractionation: unidirectional reactions in which reaction rates are dependent on the masses of the isotopes and their vibrational energies.

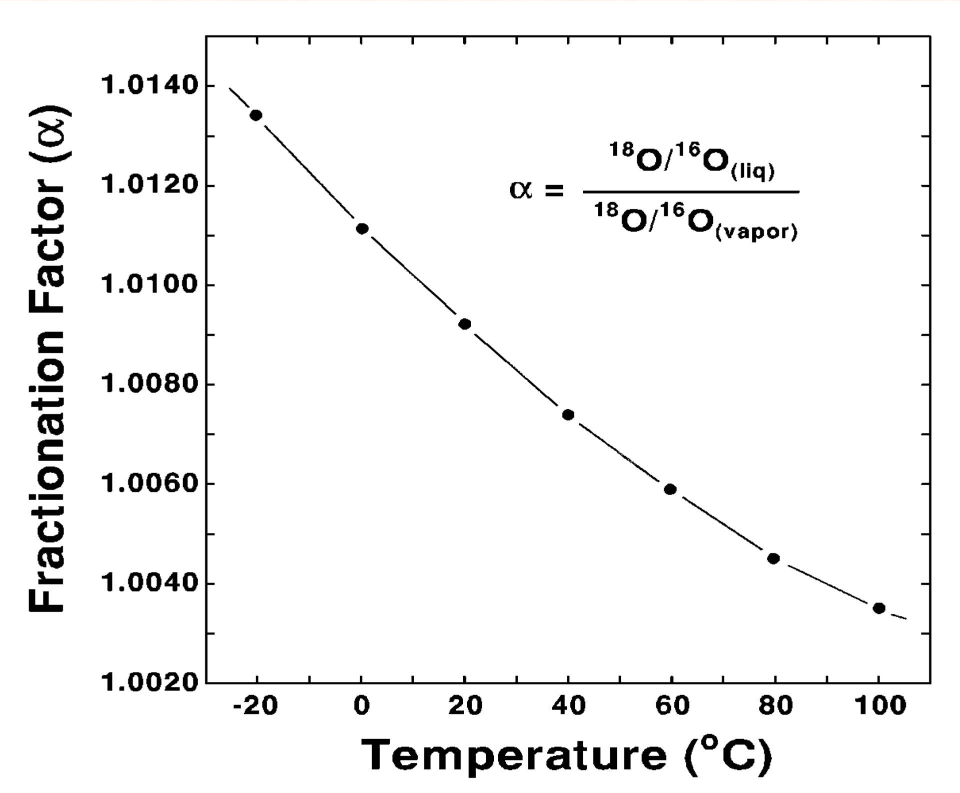
Example: breakdown of calcite in an acid solution to produce Ca^{2+} and $CO_{2\ (g)}$. The gas escapes and therefore doesn't equilibrate with the calcite.

Fractionation Factor

Describes the partitioning of stable isotopes between two substances, A and B

$$\alpha = R_A / R_B$$

where R is the ratio of the heavy to light isotope of the element for each substance and *α* is the fractionation factor



The fractionation factor varies as a function of temperature and at high temperature it approaches unity.

The δ (delta notation)

$$\delta = [(R_{samp} – R_{std}) / R_{std}] \text{ x } 1000$$

same as

$$\delta = [(R_{samp} / R_{std}) -1] \text{ x } 1000$$

Units are per mil "‰"

R is the ratio of the heavy to light isotope. Various standards are used depending on the element.

Table 6–7 Stable Isotope Ratios for Standards (Data from Kyser (1987)).

Element	Standard	Ratio
Hydrogen	V-SMOW	$^{2}H/^{1}H = 155.76 \times 10^{-6}$
Carbon	PDB	$^{13}C/^{12}C = 1123.75 \times 10^{-5}$
Oxygen	V-SMOW	$^{18}O/^{16}O = 2005.2 \times 10^{-6}$
	PDB	$^{18}O/^{16}O = 2067.2 \times 10^{-6}$
Nitrogen	NBS-14	$^{15}N/^{14}N = 367.6 \times 10^{-5}$
Sulfur	CDT	$^{34}S/^{32}S = 449.94 \times 10^{-4}$

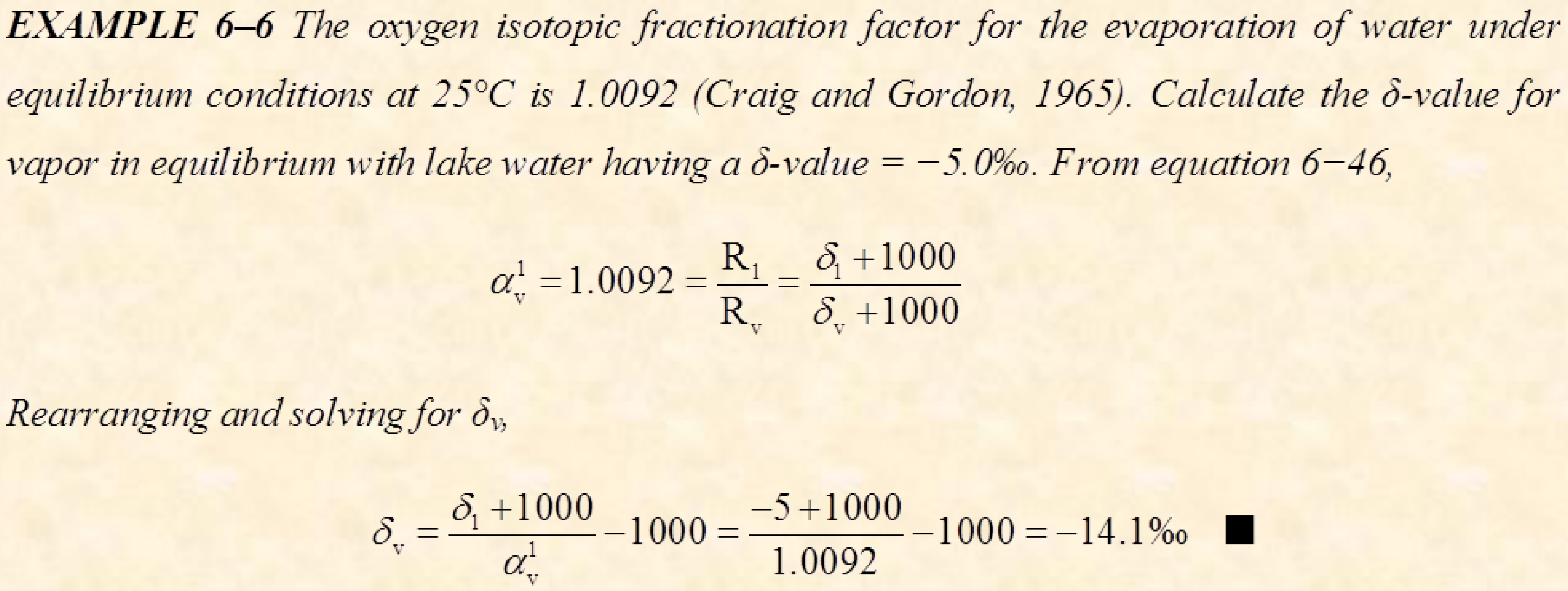
***EXAMPLE 6–5** The isotopic ratio of* $^{18}O/^{16}O$ *in V-SMOW is 0.0020052. A rainwater sample collected in Boston, Massachusetts, has an* $^{18}O/^{16}O$ *ratio of 0.0019750. Calculate the delta value for this rainwater sample.*

$$\begin{aligned}\delta &= \left(\frac{\text{Ratio}_{\text{sample}} - \text{Ratio}_{\text{standard}}}{\text{Ratio}_{\text{standard}}}\right)\times 1000 = \left(\frac{0.0019750 - 0.0020052}{0.0020052}\right)\times 1000 \\ &= -15.1‰\end{aligned}$$

The delta value is reported in parts-per-thousand (‰), and the negative value means that the sample is isotopically lighter than the standard.

Rearranging the delta-notation equation and combining it with the fractionation factor (α) equation allows for calculation of the delta value of one compartment if you know the delta value for the other compartment.

$$\alpha = R_A/R_B = (\delta_A + 1000) / (\delta_B + 1000)$$



EXAMPLE 6–6 *The oxygen isotopic fractionation factor for the evaporation of water under equilibrium conditions at 25°C is 1.0092 (Craig and Gordon, 1965). Calculate the δ-value for vapor in equilibrium with lake water having a δ-value = −5.0‰. From equation 6−46,*

$$\alpha_v^1 = 1.0092 = \frac{R_1}{R_v} = \frac{\delta_1 + 1000}{\delta_v + 1000}$$

Rearranging and solving for δ_v,

$$\delta_v = \frac{\delta_1 + 1000}{\alpha_v^1} - 1000 = \frac{-5 + 1000}{1.0092} - 1000 = -14.1‰ \quad ■$$

Oxygen and Hydrogen Isotopes in Water

Used for ‘sourcing’ water

For hydrogen we use ^{1}H and ^{2}H (deuterium, D)

For oxygen we use ^{16}O and ^{18}O

δ values for O and H in water are zero for seawater.

For water vapor in equilibrium with seawater at 25ºC - $\delta D = -69$ ‰ and $\delta^{18}0 = -9.1$ ‰

For water vapor in equilibrium with seawater at 10ºC - $\delta D = -84$ ‰ and $\delta^{18}0 = -10.1$ ‰

Temperature effects the fractionation from liquid to vapor phase for H and O. The temperature effect comes into play both for latitude and altitude. This temperature effect on fractionation is what gives rise to different isotopic values In H and O for different areas of precipitation.

The process of fractionation during condensation

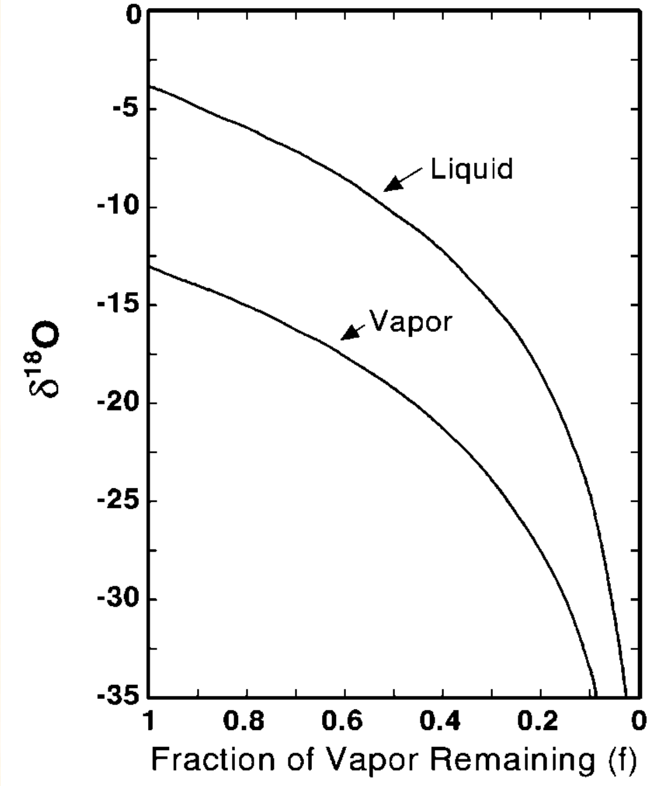
Start with water vapor that is isotopically light in H and O relative to seawater

As the vapor begins to condense out into clouds
- Initial droplets are rich in ^{18}O and D
- Vapor becomes more depleted in ^{18}O and D

As condensation continues-
- Vapor becomes more depleted
- Droplets in turn reflect lower ^{18}O and D coming from source vapor

The change in isotopic value of both the vapor and liquid is a function of how much of the original vapor is left.

Described by a Rayleigh Distillation function



Rayleigh Distillation (or fractionation)

$$\underset{\substack{\uparrow\\ \text{vapor}}}{\delta^{18}O_v} = [\underset{\substack{\uparrow\\ \text{starting}\\ \text{vapor}}}{\delta^{18}O_0} + 1000]\, \underset{\substack{\uparrow\\ \text{fraction}\\ \text{remaining}}}{f}^{\,(\alpha-1)}$$

To relate the condensing liquid to the vapor

$$\delta^{18}O_l = \alpha(\delta^{18}O_v + 1000) - 1000$$

Isotope fractionation of H and O in water (during condensation)

This process results in:

-rain early in a precip event is isotopically heavier than at the end of the event
-delta values of rain decreases from coastal to inland areas
-rain is isotopically lighter at the poles

The H and O isotopes in precipitation are related:

δD = 8 δ^{18}O + 10 (excess of D relative to ^{18}O; *d*)

or

δD = 8 δ^{18}O + d , where d is the D excess

$\delta D = 8\ \delta^{18}O + 10$

Is the equation for the Global Meteoric Water Line

This has nothing to do with meteors

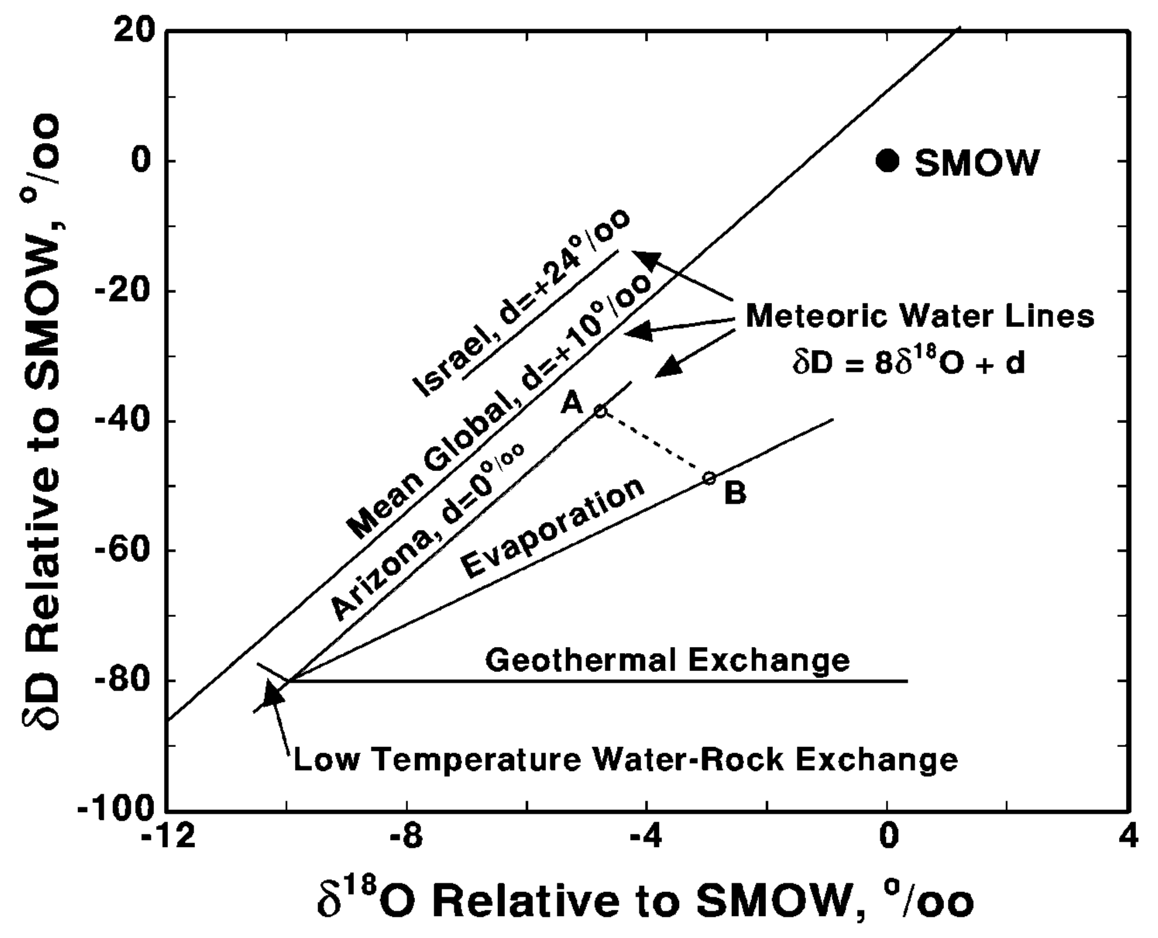


Figure 6-6. Plot of δD versus $\delta^{18}O$ illustrating the mean global meteoric water line and local meteoric water lines. Other processes that affect the isotopic ratios - e.g., low-temperature water-rock exchange, geothermal exchange, and evaporation - are also illustrated. A and B are two water masses and the dashed line represents the possible isotopic compositions of water produced by mixing of these two end members. The diagram is modified from "Uses of Environmental Isotopes" by T. B. Coplen in REGIONAL GROUND WATER QUALITY edited by W. M. Alley, pp. 227-254. Copyright © 1993. This material is used by permission of John Wiley & Sons, Inc.

Different areas influenced by evaporation, water-rock interaction, etc. will cause a deviation in the D excess (δ) relative to ^{18}O in water.

It is the different δD values relative to the GMWL that allows you to ‘tag’ water masses.

With this tag you can examine contributions of different water sources to ground and surface waters.

Example 6-7: River flow below a dam is a mixture of water coming from the reservoir behind the dam and from a groundwater source.

River…..$\delta^{18}O = -3.6$‰ , $\delta D = -44.6$ ‰
Res….. $\delta 18O = -4.5$‰ , $\delta D = -38$ ‰
GW…. $\delta 18O = -3.0$‰ , $\delta D = -49$ ‰

What's the percentage contribution of each source?

This is a two-endmember mixing problem.

For D…….$f_{GW}\, \delta D_{GW} + f_{res}\, \delta D_{res} = \delta D_{riv}$

For ^{18}O… $f_{GW}\, \delta^{18}O_{GW} + f_{res}\, \delta^{18}O_{res} = \delta^{18}O_{riv}$

2 equations, 2 unknowns,
Redefine f_{GW} in terms of f_{res},
Substitute and solve sequentially

Also $f_{GW} + f_{RES} = 1$

$f_1 = 0.40 \longrightarrow$ GW supplies 40% of the water in the river

$f_2 = 0.60 \longrightarrow$ Reservoir supplies 60% of the water in the river

Climate Change

Because the fractionation of H and O in water changes with temp, isotopic measurements of ice-cores are used to estimate paleoclimate.

1) Isotopic composition of snow reflects air temp.

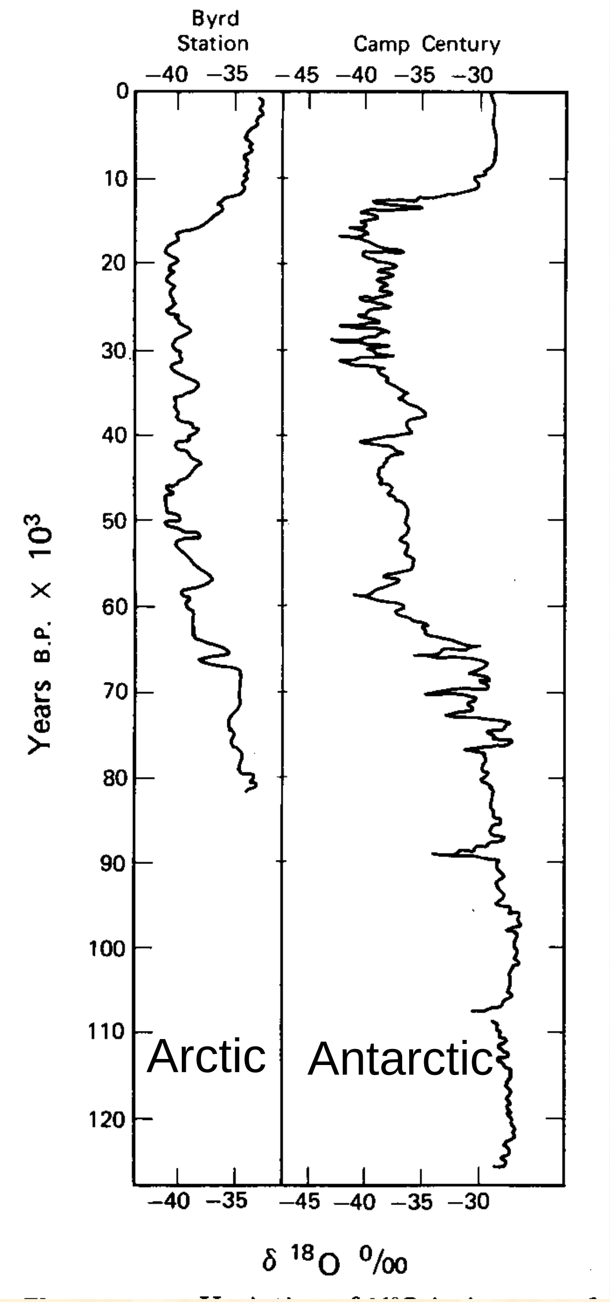
2) Colder air = more negative δD and δ^{18}O

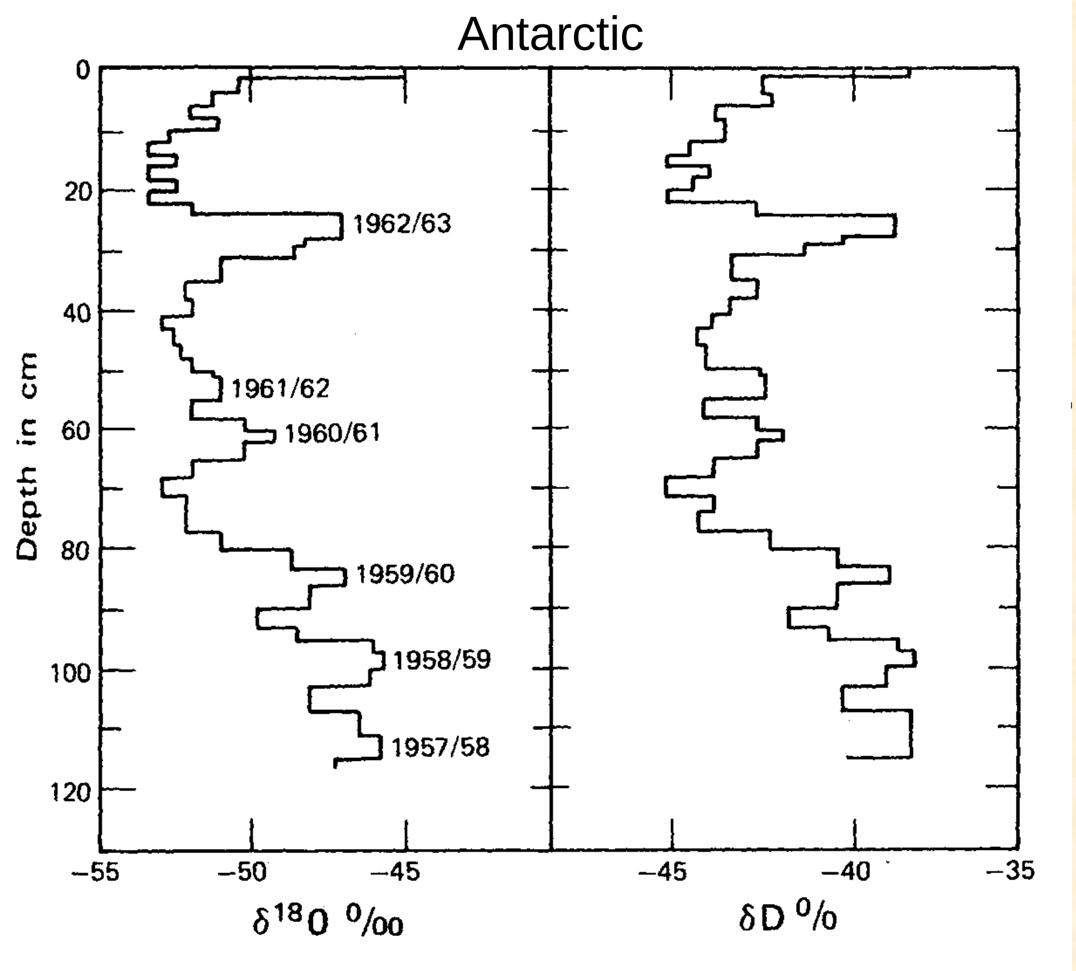
3) Warmer air = less negative δD and δ^{18}O

4) Works the same in both hemispheres

5) Once snow is packed into glacier, ice stratigraphy not disturbed, paleothermometer locked into place

   Ice ages can confound this approach to some extent because by locking up a bunch of ocean water into glaciers, the overall δD and δ^{18}O of all water gets less negative. This effect is small relative to the temp effect.



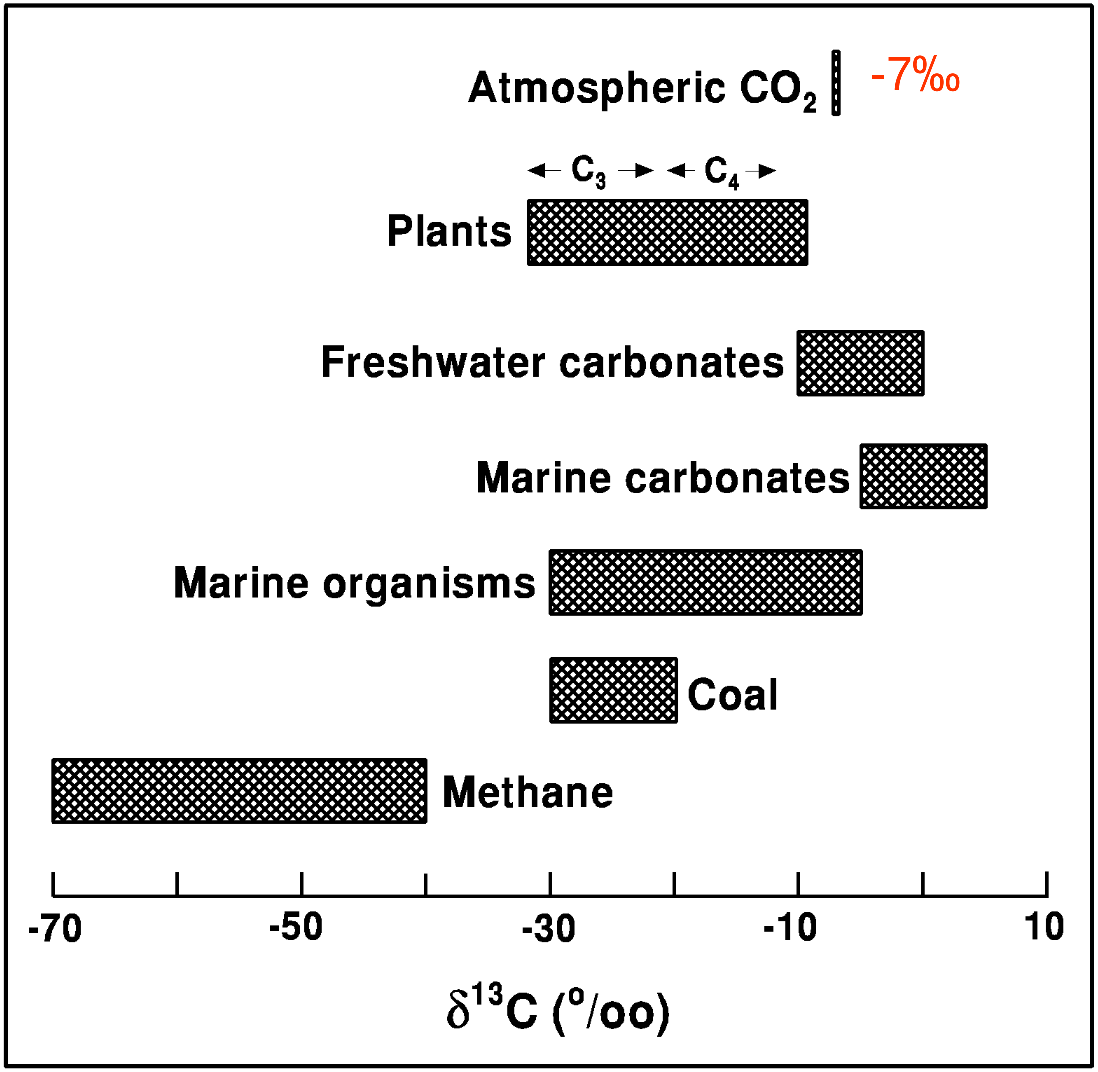


When records from both hemispheres agree, it is a global climate change

When the disagree, it is a local climate change

Carbon

We can use $\delta^{13}C$ to detect fossil fuel contributions to atmospheric CO_2. The *Suess effect*.



DIC in aqueous systems

There are isotopic fractionations associated with each step of the carbonate buffering system. *Recall from Chapter 3 that the dominant carbonate species is pH dependent.*

CO_2 gas ~ CO_2 aq

CO_2 aq → H_2CO_3

H_2CO_3 → HCO_{3-}

HCO_3- → CO_3^{2-}

CO_3^{2-} → $CaCO_3$

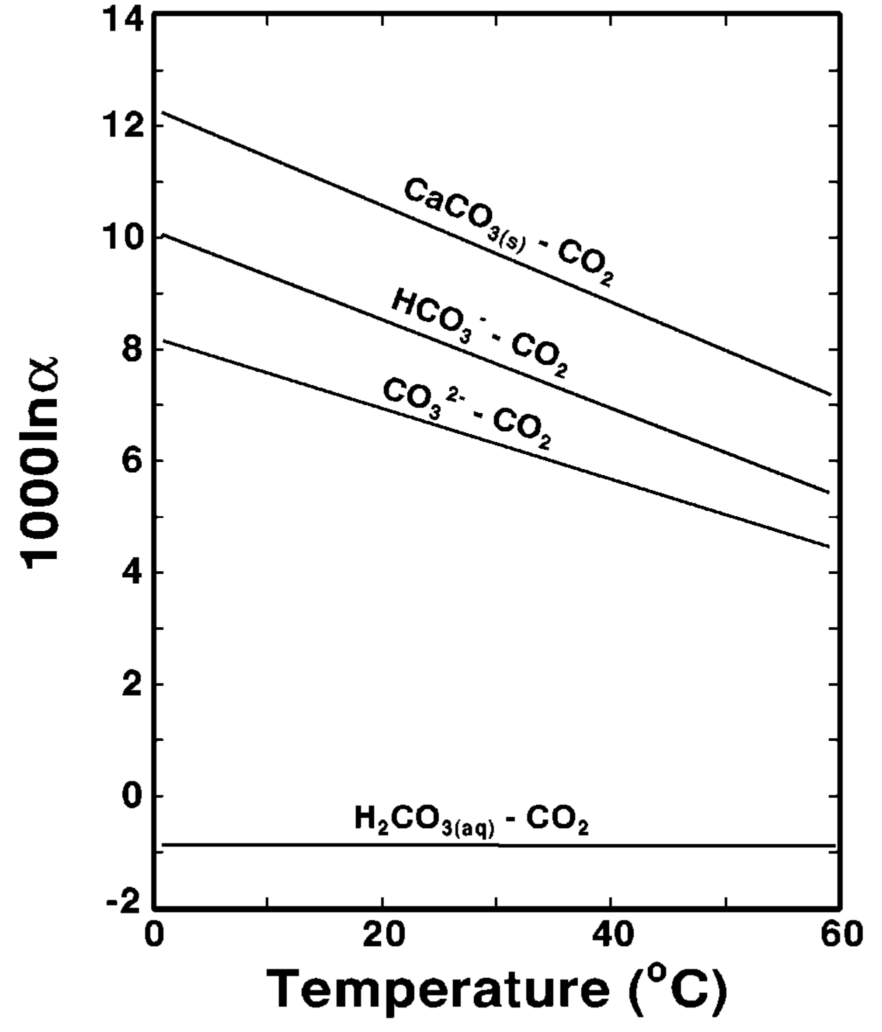
Table 6-8. Fractionation factors for carbonate species relative to gaseous CO_2*

H_2CO_3	$1000 \ln \alpha = -0.91 + 0.0063\ 10^6/T^2$
HCO_3^-	$1000 \ln \alpha = -4.54 + 1.099\ 10^6/T^2$
CO_3^{2-}	$1000 \ln \alpha = -3.4 + 0.87\ 10^6/T^2$
$CaCO_{3\,(s)}$	$1000 \ln \alpha = -3.63 + 1.194\ 10^6/T^2$

*From Deines et al. (1974).

Isotopic composition of DIC also depends on open vs closed system.

Figure 6-10. Isotopic fractionation factors, relative to CO_2 gas, for carbonate species as a function of temperature. Deines et al. (1974).



Using Equations in Table 6-8

Example 6-8: $CaCO_3$ is ppt in water in equilibrium with the atm. What is the $\delta^{13}C$ for the carbonate at 25ºC.

$CaCO_3$ relative to CO_{2g}: $1000\ln\alpha = -3.63 + 1.194 \times 10^6/T^2$

= 9.8….calcite is 9.8‰ heavier than CO_{2g}

CO_{2g} = -7‰, so calcite is 2.8‰

Example 6-9: Bicarb in ocean dominate DIC. What is the $\delta^{13}C$ for DIC in the ocean at 10ºC.

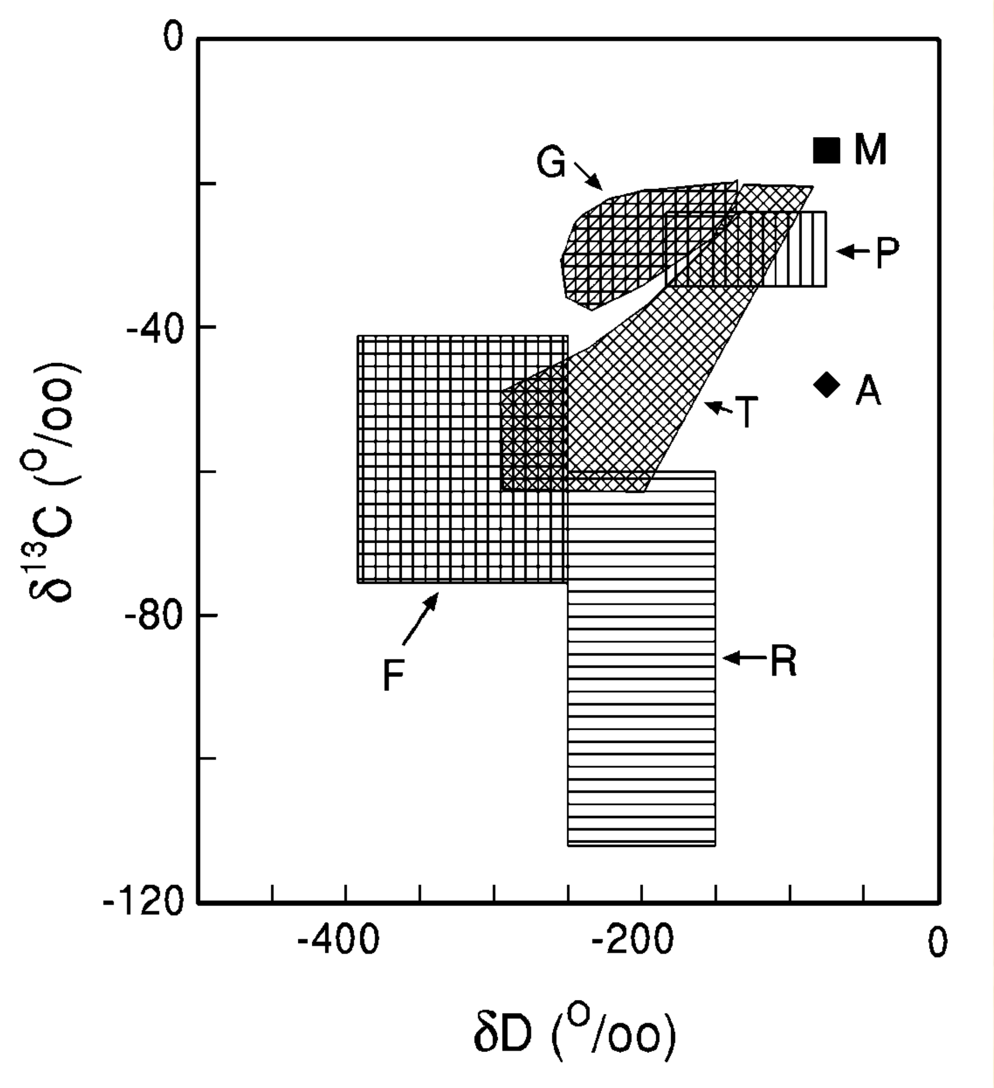
HCO_3^- relative to CO_{2g}: $1000\ln\alpha = -4.54 + 1.099 \times 10^6/T^2$

= 9.18..bicarb is 9.18‰ heavier than CO_2
Bicarb dominates DIC so …

CO_{2g} = -7‰, therefore ocean δ^{13} DIC = 2.8‰

Methane

Figure 6-11. ^{13}C and deuterium isotopic values for methane from various sources and reservoirs. M
- abiogenic (from the mantle), P - petroleum, A - atmosphere, G - geothermal (pyrolitic from interaction with magmatic heat), T - thermogenic (from kerogen at elevated temperatures), F - acetate fermentation (bacterial), and R - CO_2 reduction (bacterial). After Schoell (1984, 1988).



This technique, at least the carbon part, has been used to determine whether some deep-sea methane-based communities are fueled by thermogenic or biogenic methane deposits.

Methane hydrates, biogenic in origin

δ^{13}C average of about -65 ‰ (range -40 to -100‰)

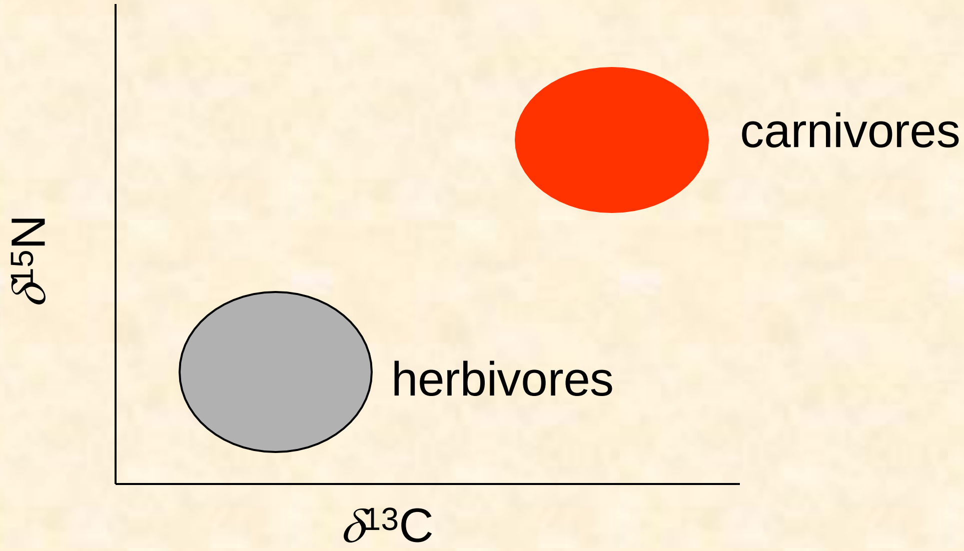
Carbon isotopes – food webs, paleo or otherwise.

C3 plants (deciduous trees) – δ^{13}C = -15‰

C4 plants (grasses, marsh, corn…) – δ^{13}C = -30‰

plankton – δ^{13}C = -22‰

Small trophic fractionation …about 1 ‰



Nitrogen

Stable isotopes of N and O used to trace sources of nitrogen pollution usually in the form of NO_3^- or NH_3

δ^{15}N can be substantially altered by biological processes

Nitrates in surface and groundwater

Fertilizer δ^{15}N = 0 ‰

Manure δ^{15}N = 15 ‰ ± 10‰

In theory you can use ^{15}N to distinguish sources. In practice, it's difficult……

Nitrate is reactive in surface and groundwaters undergoing denitrificaiton.

As denitrification converts nitrate to N_2, the residual nitrate becomes isotopically heavier. So a fertilizer source of nitrate that has undergone some denitrification will start to look isotopically like the manure nitrate.

A way to constrain this problem is to also measure δ^{18}O in nitrate

Fertilizer δ^{18}O = +23 ‰ (oxygen in nitrate comes from air)
Manure δ^{18}O = -10‰ (oxygen in nitrate comes mostly from water)

During denitrificaiton, both O and N are fractionated but their fractionations relative to each other are predictable

Red circles = measurements

Draw the predicted fractionation lines for each end-member (blue lines). Note they have the same slope

Draw a line through the measured GW sample (the mixture) that is perpendicular to the fractionation slopes (dashed line)

Now you can either do a mixing calc to determine fraction of each source, or
Amount of A = C-B /A-C
The ‘lever law’…just like torque in physics

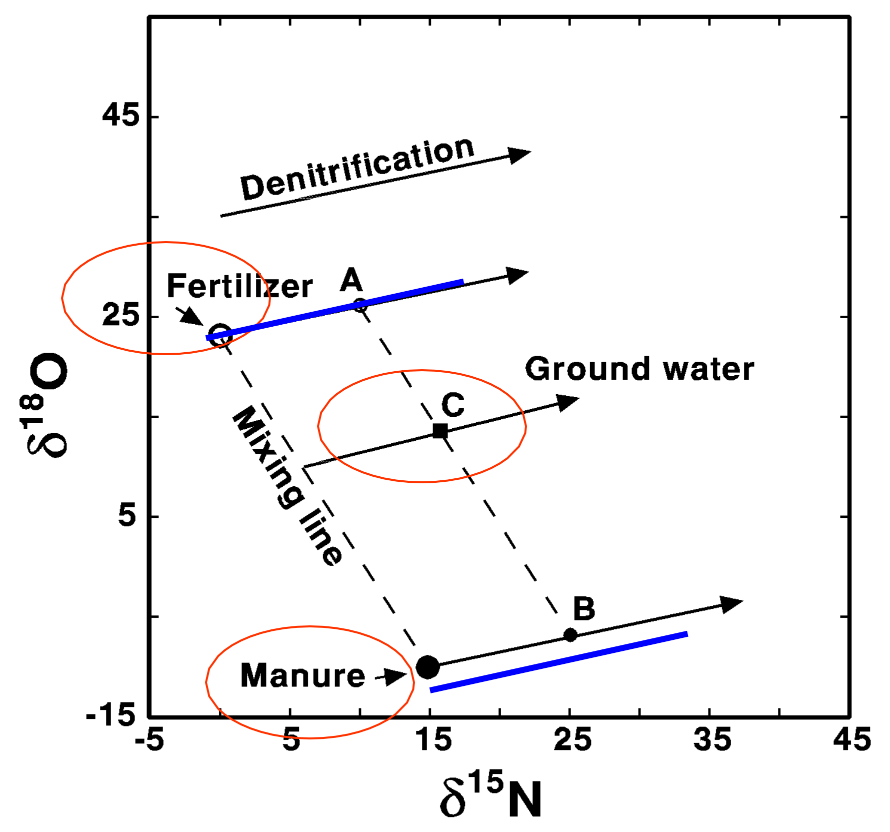
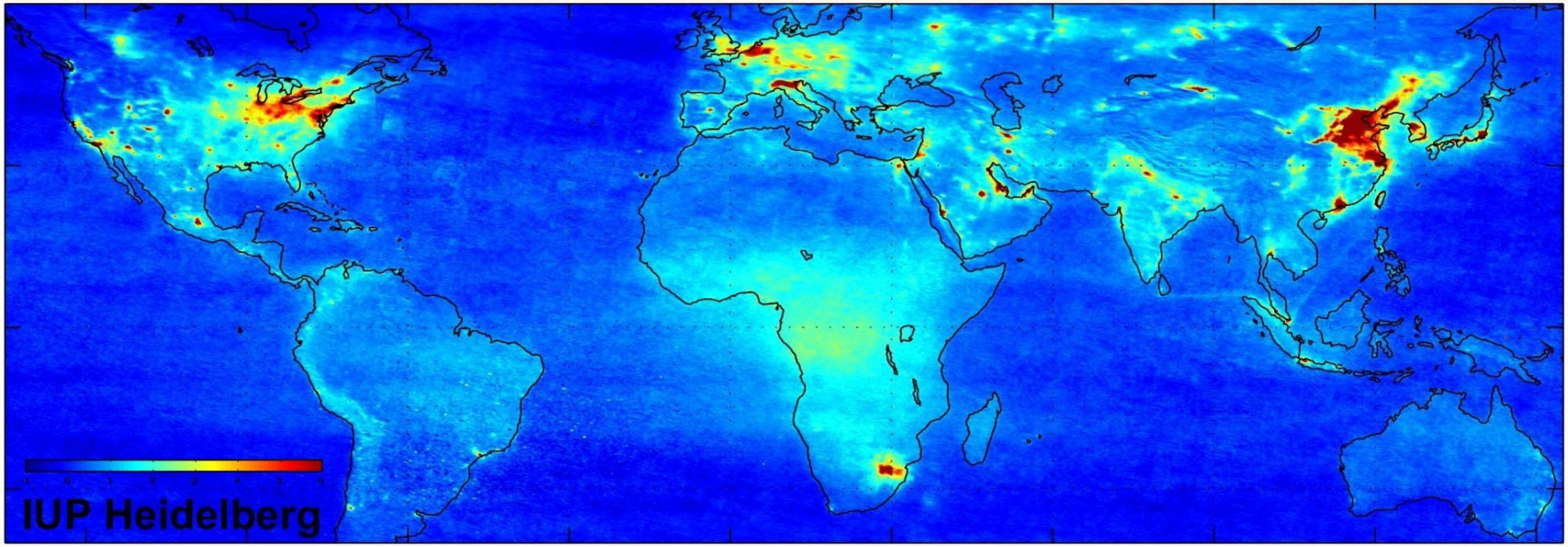


Figure 6-12. Determination of the relative importance of nitrate sources to a groundwater system. Two sources for nitrates are fertilizer and manure. Both are undergoing denitrification. A and B represent each source at a particular stage in the denitrification process. C is the isotopic composition of the nitrate in the groundwater due to simple mixing. In this example, approximately 60% of the nitrate is contributed by the fertilizer.

NH_4^+ and NO_3^- in rain

Sources of NO_x = 65% from fossil fuel
Sources of NH_4^+ = bacterial breakdown of organic matter and animal/human waste

Volatilized NH_4^+ is extremely isotopically light (30-40‰ lighter than waste)



Global NO_2 pollution

Sulfur

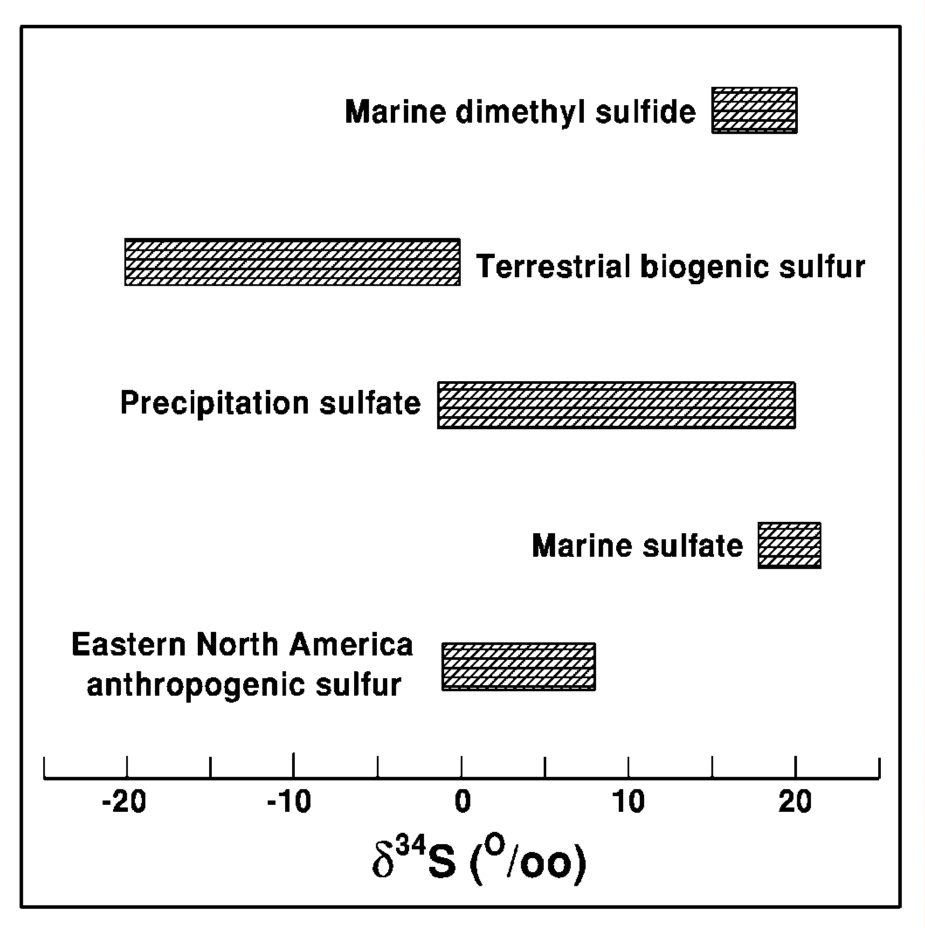
Big isotopic difference between sulfides and sulfates

Sulfate reduction (microbial) has a big fractionation, as does microbial sulfide oxidation

Is the sulfide produced during sulfate reduction isotopically lighter or heavier than the sulfate?

What’s the major source of sulfate on the planet?

Burning fossil fuels…



Mixing

Binary mixing

$$\delta_{mix} = \delta_A f_A + \delta_B (1-f_A)$$

If the two sources have unequal concentrations of the element of interest, the mixing equation must be weighted to reflect that:

$$\delta_{mix} = \delta_A f_A (A/M) + \delta_B (1-f_A)(B/M)$$

…..where A,B, and M are the concentrations
of source A, B, and the mixture with respect to the element of interest.

Mixing with more than two end members

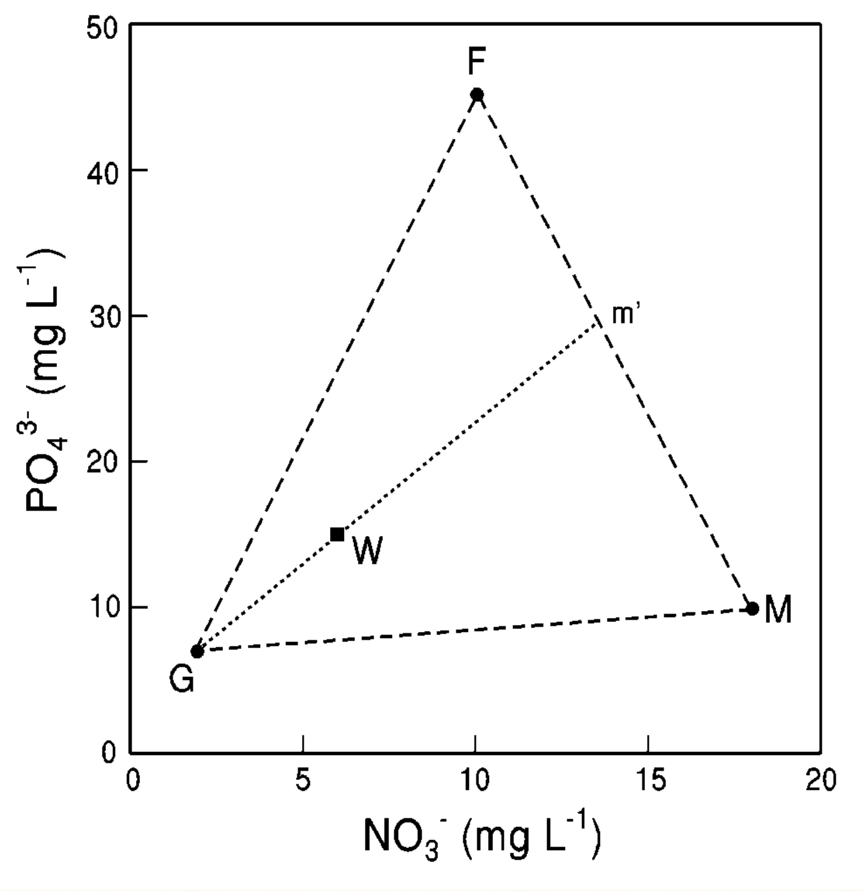


Figure 6-14. Plot of PO_4^{3-} versus NO_3^- in water samples from feedlot runoff (M), cultivated fields (F), uncontaminated groundwater (G), and contaminated well water (W). The sample of contaminated well water falls within the triangle defined by compositions M, G, and F, indicating that this sample is a mixture of these three compositions. The relative proportions of each end member can be determined by applying the lever rule (see Example 6-11).

Paleothermometry – *using carbonates*

$\delta^{18}O$ in carbonate

Fractionation factor governing water (oxygen) equilibration with CaCO3 is
temperature dependent

$$t\ (^{o}C) = 16.9 - 4.14(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.13(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2$$

Due to large and seasonal variations in freshwater oxygen isotopes, only oceanic carbonate organisms work.

Lots of other assumptions and corrections so the tool is used as a relative indicator of paleotemperature.